VESIENTUTKIMUSLAITOKSEN JULKAISUJA
PUBLICATIONS OF THE WATER RESEARCH INSTITUTE 63

JOUKO SOVERI

INFLUENCE OF MELTWATER ON THE AMOUNT AND COMPOSITION OF GROUNDWATER IN QUATERNARY DEPOSITS IN FINLAND

Tiivistelmä

Sulamisen vaikutus pohjaveden määrään ja laatuun Suomen kvartäärimuodostumissa

VESIHALLITUS — NATIONAL BOARD OF WATERS, FINLAND
Helsinki 1985

ISBN 951-46-9056-7
ISSN 0355-0982

Helsinki 1985. Valtion painatuskeskus

CONTENTS

INFLUENCE OF MELTWATER ON THE AMOUNT AND COMPOSITION OF GROUNDWATER IN QUATERNARY DEPOSITS IN FINLAND

Jouko Soveri

SOVERI, J. 1985. Influence of meltwater on the amount and composition of groundwater in quaternary deposits in Finland. Publications of the Water Research Institute, National Board of Waters, Finland, No. 63.

The network of groundwater observation stations operated by the National Board of Waters produces a body of data concerning natural variation in the quantity and quality of groundwater and factors affecting this variation.

In this study the effects of meltwater on the quantity and quality of groundwater were studied by examining input-output balances in the saturated and unsaturated soil zones. The comparison and interdependences of substance concentrations were investigated using regression analyses and other statistical methods. The cause-effect relationship between variations in groundwater quantity and quality were examined with the aid of temporal series of observations in different groundwater formation regimes. Changes occurring in meltwater during infiltration, as well as the effects of meltwater quality on groundwater acidification, were estimated in shallow aquifers.

Index words: groundwater stations, quaternary deposits, snow, infiltration, groundwater, chemical variables, deposition, geohydrological relationships, acidification.

1. INTRODUCTION

A considerable proportion of the annual precipitation in Finland falls as snow. The mean maximum water equivalent of snow cover varies from southern to northern Finland between 80 and 220 mm (Solantie 1981), representing in the south of the country 15 % and in the north about 40 % of the annual precipitation. The snow cover lasts in the south for 110 days on average and in the north for 220 days (Solantie 1977).

The water represented by the snow cover, along with various material components reaching the snow by both wet and dry deposition processes (e.g. metal ions, S and N oxidates) is rapidly released with the spring thaw into the geohydrological circulation. The late winter season and the period immediately after the spring flood generally represent the extremes of variation of the groundwater reserve in Finland.

During the winter, after freezing of the ground, the hydrogeological continuity is interrupted for a period and groundwater formation is reduced practically to zero. The groundwater level is usually at its minimum during the same period. In winter the changes in the balance of substances in

groundwater are affected mainly by the solubility of different minerals. In Finland this effect can be detected most clearly in rapakivi-granite areas, in which fluoride concentrations of groundwater always increase during periods of minimum groundwater stage (Soveri and Soveri 1981).

During the spring snowmelt the groundwater reserves are rapidly filled, usually with accompanying changes in the material budgets of the water, which may be either dilution or increase in concentration.

In Finland and in the other Nordic Countries, but especially in Canada and in the northeastern United States, sudden snowmelt and massive acid doses often occur in the spring. This phenomenon is known as the spring pH depression in surface waters and was first described in Sweden by Oden (1968).

At present and in the near future, acidification of the environment is a severe environmental problem in industrialized parts of the world. Areas having granitic bedrock, shallow and slowly weathering soils and waters with low buffering capacity have been shown to be most sensitive to acid rain. Many of these areas have been found to be particularly sensitive during the spring, when a plug of pollutants accumulated in snow during the winter months is mobilized within the snowmelt (Thornton and Eisenreich 1981).

The concentration of toxic metals in drinking water can increase due to several processes, e.g.:

— deposition of metals in soluble forms (e.g. mercury, cadmium)
— leaching of metals from the sediments (e.g. aluminium)
— corrosion of materials used in reservoirs and drinking water distribution systems (e.g. copper).

No clear evidence of health effects from the consumption of drinking water contaminated with metals resulting from acidic precipitation has yet been reported. But because some potential problems e.g. increased mobilization of harmful substances in drinking water (leaching from watershed and corrosion) have been identified this subject requires more attention and research.

A principal objective of this study was to measure the fluxes of the major dissolved substances in the snowpack — soil — groundwater system in different geohydrological and climatological conditions. The main objectives to investigate were:

— chemical composition of snow and its regional variations
— infiltration and formation of groundwater
— changes in substance concentrations of snowmelt water during the period of infiltration
— temporal variations in and interdependencies of the amount and quality of groundwater
— material balances of snowmelt water, infiltration water and groundwater
— acidification processes of groundwater

These considerations constitute important basic data in the development of water supply, particularly in sparsely populated areas, where drinking water must often be taken from well-graded soils.

The research data was mainly obtained from altogether 54 groundwater observation stations of the National Board of Waters during the period 1976—1981. The data has in some cases been complemented by snow and infiltration observations made in 1982, 1983 and 1984.

2. RESEARCH METHODS AND DATA PROCESSING

2.1 Areas studied and their hydrogeological representativity

The groundwater observation stations of the National Board of Waters are background stations in nearly natural state, located in areas where the groundwater quality has not been appreciable affected by local environmental disturbances. The stations are situated in different climatological and soil type regions and are hydrogeologically unified groundwater basins or distinct, defined areas within larger basins. The size of the areas investigated varies between 0.2 and 3.0 km^2 (Soveri 1975).

The groundwater observations were representative of the whole recharge area investigated, meaning that the hydrogeological quality and quantity parameters could be calculated from the balances of water and materials (Fig. 1).

The groundwater stations were built on different soil-type regions. The areas were also classified with regard to land use and vegetation. The structure and stratification of the soil was investigated in conjunction with the fitting of the groundwater observation tubes by profile drilling. The main directions of flow of groundwater in the different areas were estimated with the aid of surface topography formations and by measuring the groundwater level.

Textural and geological grouping of the areas was carried out on the basis of geotechnical soil type classification (Korhonen and Gardemeister

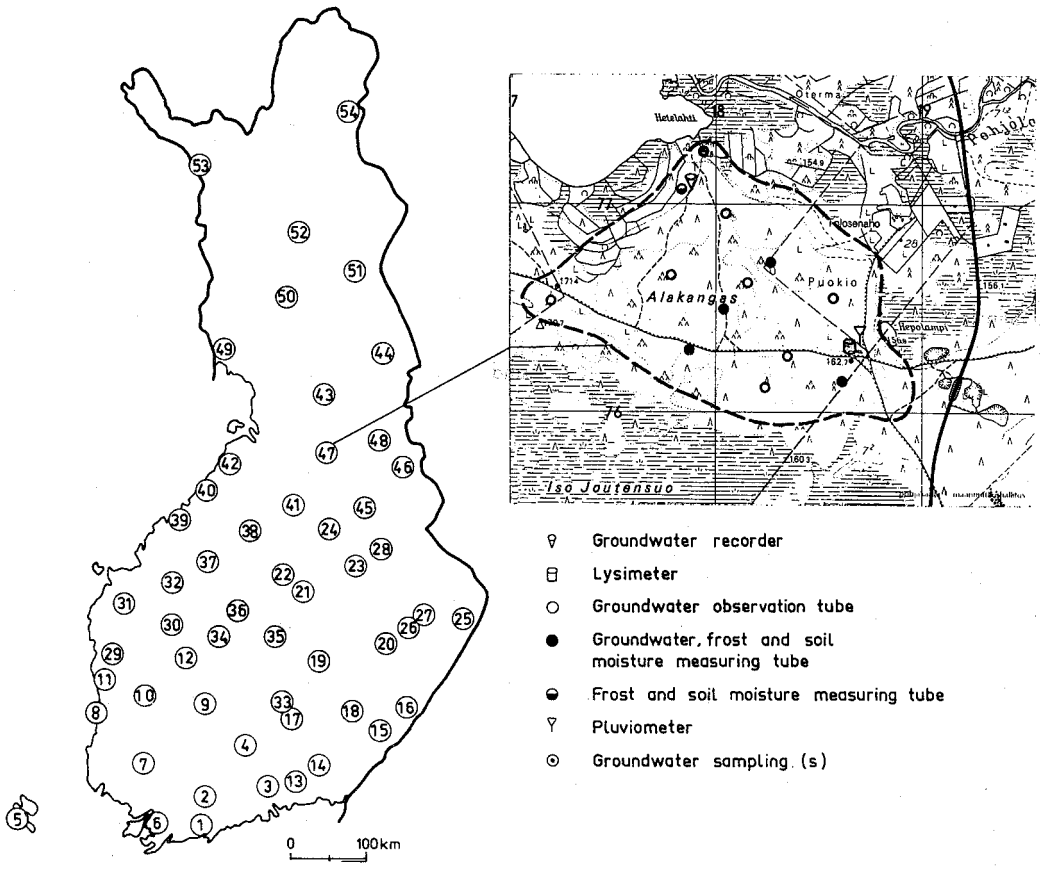

Fig. 1. The network of groundwater observation stations of the National Board of Waters and the observational procedures at the station Alakangas (47). Names of the stations, see Table 1.

1975), where the grain-size distribution e.g. for silt is 0.002—0.06 mm, for sand 0.06—2 mm and for gravel 2—60 mm. The relative dominances of different types of bedrock were estimated with the aid of available bedrock maps (Geological Survey of Finland). The soil and bedrock classification of the groundwater stations was as follows. Numbering of stations as in Fig. 1 and in Table 1.

Soil texture:

Coarse-grained; gravel: 4, 6, 7, 19, 25, 37, 41 and 47
sand: 5, 10, 16, 18, 21, 23, 26, 29, 32, 35, 42, 50, 52 and 53

Fine-grained; silt: 2, 22, 28, 34, 39 and 40
clay: 1

Well-graded; gravelly till: 8
sandy till: 12, 27, 43, 44, 45, 46 and 51
silty till: 3, 9, 11, 13, 14, 15, 17, 20, 24, 30, 31, 33, 36, 38, 48, 49 and 54

Bedrock:

Felsic plutonic rocks; granite: 1, 2, 3, 15, 24, 28, 29, 33, 34, 35, 36, 38, 40, 41, 43, 45, 46, 47, 48, 50, 53 and 54
granodiorite: 7, 10, 12, 27, 37, and 51
quartz diorite: 25
porphyry rocks: 6 and 9

Silicic schists; mica gneiss: 4, 11, 19, 20, 30, 32 and 44
veined gneiss: 17, 18, 21 and 23
mica schist: 16, 26, 39, 42, 49 and 52

Mafic rocks; amphibolite: 1 and 31
diorite: 22

Miscellaneous rocks; rapakivi-granite: 5, 13, 14 and 15
arkose sandstone: 8

Table 1. Characteristics and descriptions of the groundwater stations and the observations made. Numbering of stations as in Fig. 1. (c = cultivated land, p = peat land, f = forest, s = spring, t = tube, w = well)

Groundwater station	No	Location		Mean altitude	Soil type	Land use	Observations started			Sampling
		Lat.	Long.	m a.s.l.			Snow	Lysimeter	Groundwater	
Siuntio	(1)	60°09′	24°15′	10	sand, clay	c	1976	1981	1977	s
Karkkila	(2)	60°33′	24°13′	95	silt	f, c	1976	—	1978	s
Orimattila	(3)	60°44′	25°50′	65	silt	f, p, c	1976	—	1978	s
Tullinkangas	(4)	61°11′	25°13′	162	sand, gravel	f	1976	1978	1970	s
Jomala	(5)	60°07′	19°47′	10	sand	f, c	1976	1981	1978	w
Perniö	(6)	60°12′	22°57′	65	sand, gravel	f, p	1976	1983	1983	t
Oripää	(7)	60°55′	22°41′	85	sand, gravel	f	1976	1974	1973	t
Kuuminainen	(8)	61°30′	21°31′	7	till	f	1976	1977	1977	w
Orivesi	(9)	61°40′	24°19′	135	till	f	1976	—	1976	t
Jämijärvi	(10)	61°46′	22°47′	140	sand, gravel	f	1976	1976	1976	s
Siikainen	(11)	61°52′	21°52′	20	till	f, p	1976	—	1977	t
Virrat	(12)	62°14′	23°49′	130	till	f, p	1976	—	1976	t
Elimäki	(13)	60°45′	26°30′	55	till	f, p	1976	—	1978	t
Valkeala	(14)	60°55′	27°02′	75	sand	f, p	1976	1978	1978	s
Kotaniemi	(15)	61°23′	28°41′	100	till	f	1976	—	1976	s
Parikkala	(16)	61°37′	29°26′	90	sand	f	1976	1976	1975	s
Pertunmaa	(17)	61°31′	26°34′	115	silt	f	1976	1980	1975	w
Pistohiekka	(18)	61°34′	28°01′	85	sand	f	1976	1975	1974	w
Naakkima	(19)	62°13′	27°08′	115	sand, gravel	f	1976	1980	1975	t
Heinävesi	(20)	62°25′	28°58′	105	till	f, p	1976	1982	1974	w
Talluskylä	(21)	63°06′	26°56′	120	sand	f	1976	1980	1974	t
Viinikkala	(22)	63°16′	26°20′	115	fine sand	f	1976	1980	1974	s
Kangaslahti	(23)	63°25′	28°05′	130	sand	f	1976	1976	1974	s
Akonjoki	(24)	63°50′	27°29′	145	sand	f, p	1976	1980	1974	t
Kuuksenvaara	(25)	62°39′	31°01′	155	sand	f	1976	1975	1974	t
Jaamankangas	(26)	62°40′	29°43′	105	sand	f	1976	1975	1973	s
Jakokoski	(27)	62°44′	29°58′	145	till	f	1976	1981	1973	t
Juutilankangas	(28)	63°35′	28°57′	125	fine sand	f, c	1976	1975	1975	s
Rajamäki	(29)	62°16′	21°55′	135	till	f	1976	1980	1975	t
Taipale	(30)	62°35′	23°20′	115	till	f	1976	—	1974	s
Laihia	(31)	62°52′	22°07′	35	silt	c, f	1976	1983	1975	t
Lummukka	(32)	63°08′	23°23′	80	sand	p, f	1976	1980	1973	t
Mutkala	(33)	61°44′	26°12′	100	till	f	1976	1980	1974	w
Vehkoo	(34)	62°30′	24°42′	150	till	f, p	1976	1975	1974	s
Äijälä	(35)	62°32′	26°01′	110	sand	f, c	1976	1974	1974	s
Taikkomäki	(36)	62°50′	24°57′	180	till	f, p	1976	1980	1974	s
Halsua	(37)	63°24′	24°17′	155	sand	f, p	1976	—	1974	s
Haapajärvi	(38)	63°47′	25°16′	105	till	f	1976	1981	1975	s
Kälviä	(39)	63°52′	23°25′	15	silt, till	c, f	1976	1980	1976	t
Kalajoki	(40)	64°15′	24°03′	30	fine sand	f, p, c	1976	1980	1975	t
Pyhäntä	(41)	64°05′	26°40′	175	sand	f	1976	1982	1975	s
Turtakangas	(42)	64°36′	24°47′	80	sand	f	1976	1975	1974	s
Pudasjärvi	(43)	65°24′	27°33′	215	till	f, p	1976	1984	1974	s
Kuusamo	(44)	65°55′	29°11′	270	till	f, p	1976	1975	1974	s
Kolmisoppi	(45)	64°02′	28°32′	190	till	f	1976	1979	1975	s
Lumiaho	(46)	64°32′	29°39′	205	till	f	1976	1979	1975	s
Alakangas	(47)	64°41′	27°23′	165	sand, gravel	f	1976	1975	1975	s
Kullisuo	(48)	64°49′	28°56′	200	till	f	1976	1979	1975	s
Könölä	(49)	66°00′	24°28′	45	till	f	1976	—	1974	s
Lautavaara	(50)	66°38′	26°23′	175	sand	f	1976	1979	1974	s
Vallovaara	(51)	66°51′	28°26′	200	till	f, p	1976	1980	1974	s
Sodankylä	(52)	67°23′	26°38′	180	sand	f	1976	1979	1974	s
Muonio	(53)	68°08′	23°21′	250	sand	f	1976	1980	1974	s
Nellim	(54)	68°52′	28°17′	125	till	f, p	1976	1979	1974	w

2.11 Meteorological conditions

Wind speed and direction have a major effect on the transport of pollutants from their source to the site of deposition. With increase in wind speed the amount of air passing over a given area increases and the local levels of pollutants are diluted. As a result of this the mixing of components is more complete and they are spread to a greater distance from their source. The direction of the wind determines in which direction the pollutants are carried from their source.

The mean wind directions during the winter seasons 1975/1976 . . . 1980/1981 are presented in Fig. 2 in the form of wind roses. Each vector represents the relative proportion of the prevalence of wind direction calculated from daily observations during the winter season. The most prevailing direction is marked with an arrowhead. The data were gathered from the weather stations of the Finnish Meteorological Institute.

Weather conditions vary considerably in Finland during the winter season. Although the dominant wind direction is from south to north, several other wind directions are also significant. For this reason it is not possible to present definite trajectories for any substances on the basis of relative concentrations in snow.

Annual variation in climatic conditions was examined in the areas of Turku, Lappeenranta, Jyväskylä, Oulu and Sodankylä in the years 1976—1984 (Table 2). Data were gathered from observations of the Meteorological Institute and of the

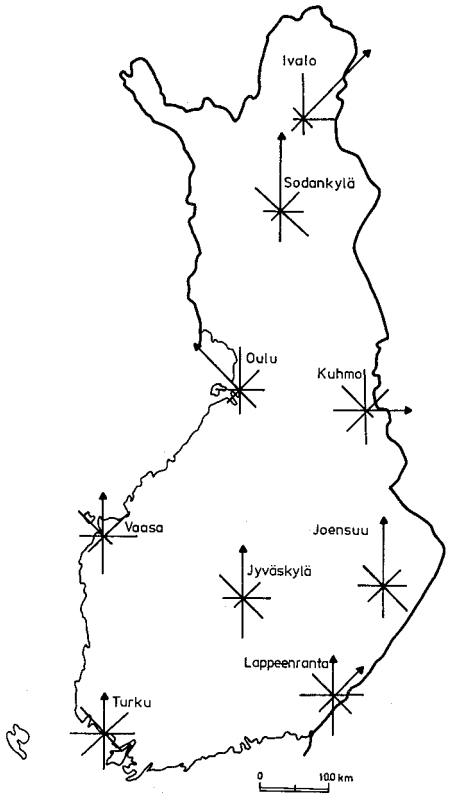

Fig. 2. Prevailing winds during the winter seasons 1975/1976 – 1980/1981 at the weather stations of Turku, Vaasa, Lappeenranta, Jyväskylä, Joensuu, Oulu, Sodankylä, Kuhmo and Ivalo.

Table 2. Values of maximum water equivalent of snow (We_{max}), annual precipitation (P_a) and mean air temperature (T) for 1976—1981 along with the corresponding long-term means for the period 1961—1975.

Area	Variable	Years									Period
		1976	1977	1978	1979	1980	1981	1982	1983	1984	1961—1975
Turku	We_{max}	110	116	71	102	38	115	147	37	100	105
	P_a	455	810	590	670	790	830	650	720	880	610
	T	3.8	4.5	3.6	4.5	4.6	4.5	5.3	5.7	5.8	4.9
Lappeenranta	We_{max}	125	105	114	90	145	225	175	110	220	144
	P_a	435	690	475	695	685	900	583	718	746	600
	T	2.2	3.3	2.1	3.5	3.1	3.5	3.8	4.5	4.5	3.7
Jyväskylä	We_{max}	111	133	94	110	116	241	131	98	202	132
	P_a	520	740	420	720	620	850	580	730	615	660
	T	1.3	2.5	1.3	2.8	2.2	2.4	2.9	3.4	3.6	2.9
Joensuu	We_{max}	105	110	85	90	115	224	165	155	230	150
	P_a	455	575	455	540	660	750	609	767	672	570
	T	0.6	2.2	0.7	2.4	1.7	2.1	2.4	3.0	3.4	2.4
Oulu	We_{max}	92	120	82	79	66	178	126	126	130	98
	P_a	385	520	360	600	450	690	442	679	517	530
	T	0.9	1.8	0.8	2.1	1.4	1.2	2.4	2.5	3.0	2.2
Sodankylä	We_{max}	153	206	160	119	198	226	157	169	175	161
	P_a	390	520	410	544	415	620	459	551	506	515
	T	−1.8	−1.5	−2.3	−0.8	−2.0	−2.4	−0.4	−0.8	0.0	−0.8

hydrological office of the National Board of Waters.

The maximum values of the water equivalent of snow, the uncorrected figures for annual precipitation and the mean annual air temperature all varied considerably between the regions in different years. Unusually low rainfall was recorded in 1976 and 1978, whereas high levels of precipitation were recorded throughout the country in 1981, particularly during the winter months. The deviation of climatic conditions from the mean was also examined by comparison with the mean conditions for the years 1961—1975.

2.2 Analysis programme

The quality parameters determined of snow, infiltration water and groundwater, along with the numbers of observations, are presented in Table 3.

A rather large number of the components determined were present in relatively high concentrations in the mg l^{-1} range. Other components, such as the heavy metals, were present as trace constituents at or even below the $\mu g\ l^{-1}$ level.

The sensitivity of water analysis has developed rapidly in recent years. For example, during the period of this research the detection limits of some of the heavy metals improved by a factor of ten or even one hundred. In some cases this has made the comparison of results rather difficult.

Particular attention was paid during the study to the representativity of samples. Contamination in conjunction with sampling, sample handling and the actual site of sampling itself may be of particular significance in the case of analysis of components present only in very low concentrations. The field observations, sampling, sample handling and analyses were all carried out in accordance with current instructions in the National Board of Waters (Erkomaa and Mäkinen 1975, Vesihallitus 1984a).

The analyses were performed as soon as possible after sampling. The samples were preserved for analysis according to normal practice as follows:

500 ml (No preservation): SO_4, Na, K, Ca, Mg, F
100 ml (1 ml l + 1 HNO_3); Zn, Cu, Pb
250 ml (2.5 ml 8 N H_2SO_4); Al

Table 3. The amount of determinations (n) made of snow (SW), infiltration water (IW) and groundwater (GW) during the period 1976—1981.

Parameter	Symbol	Unit	Amount of determinations		
			SW	IW	GW
pH-value			286	65	2444
Electrical conductivity	γ_{25}	mS m^{-1}	291	64	2389
Calcium	Ca	mg l^{-1}	284	53	2220
Magnesium	Mg	mg l^{-1}	283	54	2271
Sodium	Na	mg l^{-1}	281	53	2276
Potassium	K	mg l^{-1}	281	53	2247
Total nitrogen	N_{tot}	mg l^{-1}	277	64	—
Total phosphorus	P_{tot}	mg l^{-1}	275	58	2288
Chloride	Cl	mg l^{-1}	283	64	2331
Sulfate	SO_4	mg l^{-1}	275	57	2223
Copper	Cu	$\mu g\ l^{-1}$	262	49	2089
Manganese	Mn	$\mu g\ l^{-1}$	266	56	2187
Lead	Pb	$\mu g\ l^{-1}$	278	52	2052
Aluminium	Al	$\mu g\ l^{-1}$	6	28	1094
Zinc	Zn	$\mu g\ l^{-1}$	266	—	2088

2.21 Snow meltwater

Snow generally contains great many impurities which may arise from natural sources, locally created contaminants, or from long range sources of pollutants.

Snow samples were taken at the sites of the groundwater stations (Fig. 1) using plexiglass samplers (Fig. 3). The sampler was pushed vertically into the snowpack with a steady downwards thrust. Sampling was carried out according to the scheme shown in Fig. 3, and was repeated at different points within a 10 m^2 area until a sufficient volume of sample water (1.75 l) had been obtained (Vesihallitus 1984a).

From the point of view of the representativity of the snow samples it was important that they were taken from sites at which no melting had yet taken place. A considerable proportion of the materials stratified in the snow is lost during the first stages of melting. Johannesen and Henriksen (1978) reported results from both laboratory and field experiments which indicated that 44—76 % snowbound pollutants are released during the melting of the first 30 % of the snow. Snow crystals are formed in high, relatively clear air masses and pollutants are adsorbed to the surface as the snow passes through polluted air. The polluted outer surfaces thus give rise to the first meltwater (Gjessing and Gjessing 1975).

Another condition was that the snow cover at the sampling site should represent the mean snow conditions of the area. Piling up or removal of snow due to wind drifting should not have occurred. The primary representativity of the snow cover was demonstrated at the sampling site by measuring the depth of the snow or its water equivalent.

The snow samples were stored in polythen bags and transported frozen to the laboratory,

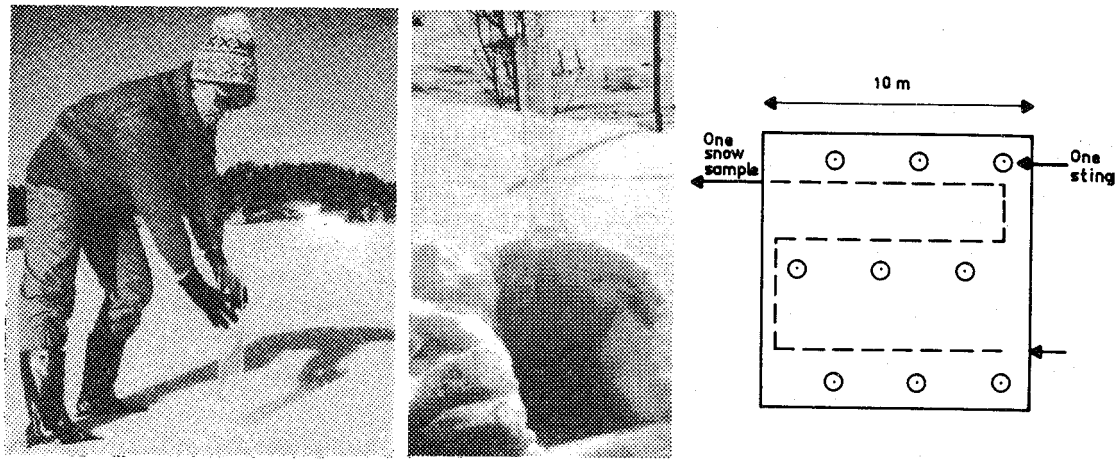

Fig. 3. Snow sampling procedures and a diagram of sampling track.

where they were melted at room temperature to a snow-water mixture in polythen beakers and homogenized prior to analysis by shaking. A total of 6 320 analyses were carried out from 486 samples over the period 1976—1984.

2.22 Infiltration water

Infiltration means the penetration of meltwater or rainwater from the soil surface into the soil. The infiltrated water flows through the soil under the action of gravity as percolation water. In the past there has been some disparity in the definition of "infiltration" and "percolation". The word "percolation" has been used to describe either the vertical movement of water in the unsaturated zone, or the nearly horizontal movement within the saturated zone. Likewise "infiltration" has been used both to refer to the movement of rain water into the soil horizon and more generally to the movement downwards to the water table (Morel and Wright 1978).

In this context water collected by the lysimeters is called for infiltration water.

Infiltration experiments were carried out using lysimeters (Fig. 4). These are zinc plate vessels, of diameter 1596 mm and depth 1700 mm, which are

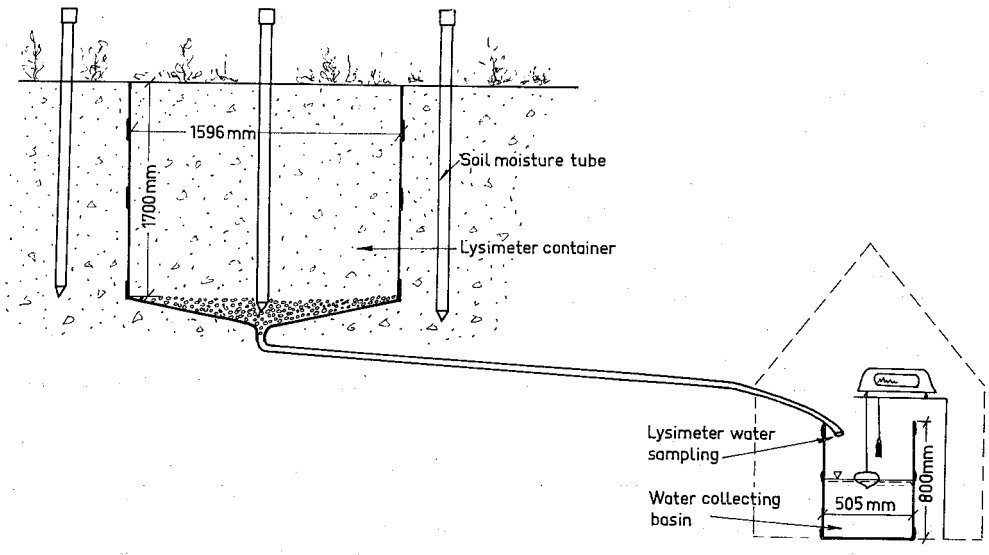

Fig. 4. Scheme of the lysimeter and the sampling of infiltration water.

buried into the soil. Both the soil type and surface vegetation in the vessels correspond to those prevailing in the area. The natural stratification and the podzol zones in lysimeter vessels are disturbed.

The amount of water filtering through the lysimeter into the collection vessel below in unit time was measured using a recorder. Results from 13 groundwater stations representing a total of 37 observation years were available. Infiltration due to meltwater and its proportion of the total annual infiltration, as well as the relationship between infiltration and the formation of groundwater, was investigated in areas with different soil types.

Infiltration water samples for chemical analysis were collected directly into polythene bottles from the mouth of the plastic connecting tube of the lysimeter. Water quality investigations of infiltration water were carried out during the period 1978—1984 from a total of 64 samples. The investigations of water quality were carried out in both coarse sediments and in till soils.

Zinc was not analyzed at all, due to the danger of metal contamination in the lysimeter vessel. Slight contamination was also observed in the case of copper. Clear cases of contamination were excluded from the data.

2.23 Groundwater

The groundwater means the subsurface water in the zone of saturation, having a hydrostatic pressure equal or higher than atmospheric (Johansson 1984 ed.).

Groundwater samples were taken from the permanent observation stations either from springs or from PVC sampling tubes fixed in the soil (see Table 1). In order to monitor seasonal changes and to facilitate the comparison of results from different sites, samples were taken regularly during the last week of each month from a fixed depth and using the same standardized sampling procedure (Soveri 1980). A total of about 55 000 analyses from almost 3 000 samples taken from 54 groundwater observation stations were carried out during the period 1976—1981.

Changes in the level of groundwater reflect the balance between its recharge and discharge. The formation of groundwater due to the spring melt was investigated at the observation stations by recording the areal means of groundwater level. Areal means in this context were specified as the means ot the groundwater level observation tubes distributed systematically over the area (see Fig. 1).

Manual measurements of groundwater level were made at 540 observation sites on the first and fifteenth days of the month. A total of about 78 000 measurements were made. In addition, data from continuous recording of groundwater level was available from the permanent groundwater stations. This data consisted of a total of about 120 000 daily observations. The recorder data were used in order to determine accurately the time during which groundwater was formed due to snowmelt. The increase in groundwater level represents the period during which mixing of meltwater and groundwater occurred.

2.3 Processing of the data

The results of the analysis of snow, infiltration water and groundwater samples are stored in the registers of the National Board of Waters. The statistical analysis of the data was carried out using the computer of the National Board of Waters and commercially available Biomedical Computer Programs (BMDP 1983).

In addition to the statistical results, the correlations between different material concentrations and the frequency distributions of individual materials were printed out in the form of data matrices. Regression functions, correlation coefficients and significance levels were calculated for the pairs of variables having the strongest interdependences.

Statistical examination of the regional concentrations was carried out on the basis of the 13 Water Districts of the National Board of Waters.

The areal means of groundwater height were calculated manually from the water level data of the observation tubes. Infiltration volumes were calculated from the recorder curves of the lysimeters.

3. MATERIAL CONCENTRATIONS AND THEIR AREAL DIFFERENCES IN THE SNOWPACK

Materials present in snow reflect the level of air pollution. Atmospheric constituents which find their way into rain and snow originate from five major sources:

— wind suspension of mineral and organic dust
— sea spray

— volcanism
— gas emanation from bedrock, drift and vegetation
— anthropogenic emissions

The first four sources can collectively be called natural sources. Anthropogenic emissions contribute significantly to the trace metals and acid content of rain and snow (Thornton and Eisenreich 1981). Garrels et al. (1975) calculated the ratio between airborne emissions due to human activity and those due to natural causes for twelve toxic metals. These ratios, known as "global atmospheric interference factors" are: for mercury (80), lead (70), molybdenum (29), antimony (28), selenium (14), cadmium (5.2), zinc (4.6), tin (3.5), arsenic (3.3), copper (2.3), vanadium (1.3) and nickel (0.9).

Snow may store and after melting suddenly release great amounts of chemicals. The movement of impurities with water inside snow has not been investigated as thoroughly as the movement of water itself. In general, two types of mixing occur as impurities move with meltwater through the snow:
— molecular diffusion
— mechanical dispersion (Colbeck 1981).

A simple model for pollutant concentrations during snowmelt was evaluated by Hibberd (1984). After him the percolation of meltwater is not a homogeneous process; meltwater often follows preferred channel through the snowpack rather than percolates downwards as a uniform front of water.

No systematic study of the material contents of snow on a nationwide basis has hitherto been carried out in Finland. Viro (1953) conducted investigations of snow and rainwater during the years 1952—1953 but his results are not directly comparable with those of the present investigation due to differences between the methods used. Comparable results for snow have been published in Norway and Canada since 1960s' (e.g. Elgmork et al. 1973, and Wright and Dovland 1978).

In the comparison of substance budget between snow, infiltration water and groundwater, results of the concentration in the snow were utilized directly. Increases in concentrations due to evaporation were not taken into account, because the significance of it during the spring thaw is rather small. According to Kuusisto (1984), evaporation accounts for only about 5 % of the thaw.

The snow cover forms a natural base for the deposition of various materials, upon which air pollutants are accumulated stratigraphically.

Loading originating from the atmosphere was estimated individually for each constituent from the snowmelt water. The analysis results of the snow itself were expressed as monthly deposition during the winter season (mg m^{-2} $month^{-1}$) with the aid of the water equivalent data relating to the deposition.

The deposition describes the local material loading as a function of time and surface area. The material concentrations of snow were converted to mean monthly deposition values representing a particular winter with the aid of equation (1):

$$D_m = \frac{30\ We}{\Delta D_t} \cdot C_s \qquad (1)$$

where
D_m = monthly deposition (mg m^{-2})
C_s = snow bulk concentration (mg l^{-1})
We = water equivalent of snow (mm)
ΔD_t = time of deposition (in days)

The regional water equivalent data of snow were obtained from the monthly data sheet of the hydrological office of the National Board of Waters (Hydrological yearbooks 1976—1981) and the durations of permanent snow cover from the daily observations of the Finnish Meteorological Institute.

3.1 Chemical variables in snow

3.11 Acidity and electrical conductivity

The *pH value* of rainwater in Finland varied between 4.4 and 5.7 during the period 1971—1977. The rainwater and snow cover were markedly more acidic in the southwest than in the remainder of the country. The distributions of about 3000 values of rainwater pH and 286 of the pH of snow cover with respect to the pH value of 4.6 were as follows:

pH	Rainwater	Snow
> 4.6	61 %	46 %
4.6	15 %	14 %
< 4.6	24 %	40 %

In Finland the concentration of hydrogen ions corresponding to the average pH of rainwater of 4.8 is about 35 μ mol l^{-1}. This is e.g. higher than the corresponding figure for Norway of 25 μ mol l^{-1} (Soveri 1982 ed.).

Acid rain is usually episodic in its occurrence. The lowest pH value of rain ever measured in Finland was 2.92 at a background observation station at Joroinen in 1977. This pH value corresponds to a hydrogen ion concentration of

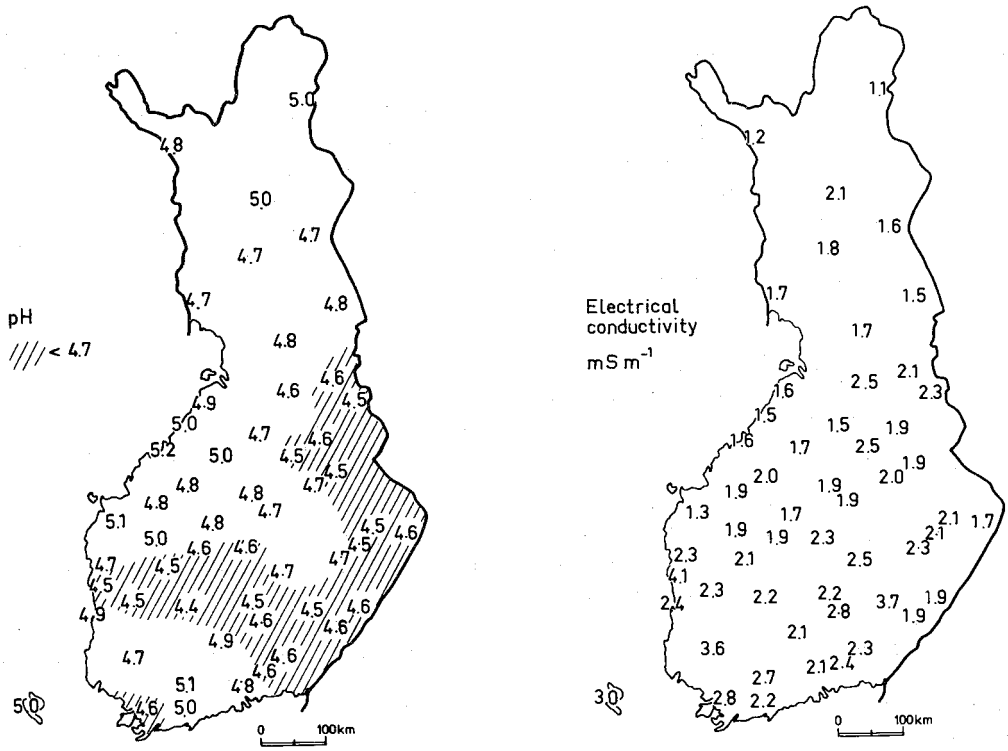

Fig. 5. Median values of the pH and mean values of the electrical conductivity of snowpack during the period 1976–1984 at the observation stations (Fig. 1 and Table 1) of National Board of Waters.

almost 1 500 μ mol l^{-1} (Kulmala et al. 1982).

The pH of pure rainwater or snow in equilibrium with the carbon dioxide of the air is about 5.6. Thus rain or snow with a pH below this value can be considered as acidic. Of the Nordic Countries the pH of precipitation is close to this value (5.5—5.6) only in Iceland (Soveri 1982 ed.). During the period 1976—1981 the snow samples studied in Finland (= 286) had a pH range of 3.7—6.2 with a median value of 4.6 (Fig. 5).

Regional variations in the pH values of snow between the northern and southern parts of Finland are rather small. However, the zone with the lowest median value of pH is clearly in the south. The pH value of snow was also exceptionally low in southeastern and eastern Finland.

The four ions usually of most importance to rainfall acidity are: hydrogen (H^+), ammonium (NH_4^+), nitrate (NO_3^-) and sulfate (SO_4^{2-}). Other ions (e.g. calcium) may be important under some conditions. Some of the nitrogen and sulfur-containing pollutants are oxidized to nitric and sulfuric acids, so that the acid content of precipitation is mainly a secondary result of the primary emissions (Bangay and Riordan 1983).

The phenomenon of acidic precipitation, commonly known as acid rain, is acknowledged to be one of the most pressing current environmental issues. Man-made atmospheric pollutants are probably the major contributions to acid deposition especially in the Nordic Countries. In addition, natural sources of acid precursors are also known to exist.

The major reason for the acidification of precipitation is the liberation of oxides of sulfur (SO_2) and nitrogen (NO_x) to the atmosphere in conjunction with the combustion of fossil fuels. It has been estimated that approximately half the sulfur in the atmosphere on a global scale originates from natural emissions (NAPAP 1983). Ammonia, as well as alkaline dust and other particles of natural origin, can neutralize and offset the effects of acid rain.

The total concentration of ionizing salts in snow, determining the *electrical conductivity* of the melted water, reflects the amount of salts descending from the atmosphere, with deposition. Increase in acidity is also accompanied by an increase in electrical conductivity.

During the winter seasons 1976—1981 the

conductivity of snow was between 0.6 and 8.9 mS m^{-1}. The mean conductivity value for different years varied between 1.1 and 3.7 mS m^{-1} (mean 2.2 mS m^{-1} and median 2.1 mS m^{-1}) (Fig. 5).

Clear regional differences in electrical conductivity values were recorded between the industrial south of the country and the sparsely populated areas of the north.

3.12 Alkali and earthalkali metals

The concentrations of alkali and earthalkali metals in rainwater are affected in summer by the proximity of the sea (Järvinen and Haapala 1980). During the winter the effect of the sea is only slight in the Finnish climate.

The concentrations of calcium, magnesium, sodium and potassium in snow differed considerably. In the north, the concentrations of all four metals were lower than the average of the country. In sodium and magnesium concentrations, no clear effect of the sea was discernable (Fig. 6).

Concentrations of *calcium* in the snow varied between 0.1 and 2.0 mg l^{-1} (mean 0.4 mg l^{-1} and median 0.3 mg l^{-1}). The mean concentration corresponded to a monthly deposition of 10.7 mg m^{-2}.

The concentrations of *magnesium*, were between 0.1 and 1.6 mg l^{-1} (mean 0.1 mg l^{-1} and median 0.1 mg l^{-1}). The corresponding monthly deposition was 4.1 mg m^{-2}.

Sodium concentrations were between 0.1 and 1.7 mg l^{-1} (mean 0.1 mg l^{-1} and median 0.2 mg l^{-1}) and the corresponding monthly deposition was 7.6 mg m^{-2}.

Potassium concentrations were between 0.1 and 1.9 mg l^{-1} (mean 0.2 mg l^{-1} and median 0.2 mg l^{-1}). The mean concentration corresponded to a monthly deposition of 6.2 mg m^{-2}.

The relationships between the mean concentrations of the group of cations investigated in snow with respect to magnesium were:

$$Mg < 1.5\ K < 1.9\ Na < 2.7\ Ca \qquad (2)$$

and the corresponding relationships calculated for the depositions were:

$$Mg < 1.5\ K < 1.9\ Na < 2.4\ Ca. \qquad (3)$$

In comparison with earlier estimates of deposition (Viro 1953, Buch 1960, Järvinen and Haapala 1980), the deposition figures reached in this investigation were almost without exception smaller. Only the value for magnesium was at approximately the same level as in the earlier estimates (Table 4). The measurement results for the summer months were affected by several disturbing factors such as proximity of the sea, soil dust and pollen raised and transported by the wind, etc.

Table 4. Monthly deposition results for calcium, magnesium, sodium and potassium according to various authors.

Monthly deposition in mg m^{-2}				Reference
Ca	Mg	Na	K	
16.6	10.9	15.3	20.4	Viro (1952—1953)
30.3	3.5	13.2	8.2	Buch (1955—1958)
29.7	6.4	14.8	12.5	Järvinen and Haapala (1971—1977)
10.7	4.1	7.6	6.2	Soveri (1976—1981)

3.13 Nitrogen and phosphorus

Nitrogen and phosphorus take part in the biological cycling of materials as major nutrients. Considerable amounts of these elements enter the ground and watercourses from the air (Soveri 1980).

The total *nitrogen* concentrations of snow varied between 200 and 1877 μg l^{-1}, the mean concentration being 736 μg l^{-1}. The concentrations were considerably higher in southern Finland than in the northern part of the country (Fig. 7).

The total annual nitrogen deposition corresponding to the mean concentration of nitrogen in snow was 340 mg m^{-2}. This result is significantly lower than the estimate of 545 mg^{-2} reached by Järvinen and Haapala (1980), but on the other hand very much higher than the estimate of 60 mg m^{-2} presented by Buch (1960). The Water Research Institute has monitored the quality of precipitation at 50 sampling stations since 1971, and the deposition values of Buch were collected from sex sampling stations since 1954.

Total *phosphorus* concentrations in snow varied between 1.0 and 84 μg l^{-1}, the mean value of 18 μg l^{-1} corresponding to an annual deposition of phosphorus of 6 mg m^{-2}. The values of phosphorus deposition obtained were significantly lower than those calculated from rainwater concentrations. The summer deposition figures are exaggerated by windborne secondary particulate material and pollen. The apparent phosphorus deposition results for the summer season may be as much as double the corresponding values measured in winter (Haapala 1972).

The regional variations in total phosphorus concentrations of snow were rather small and no

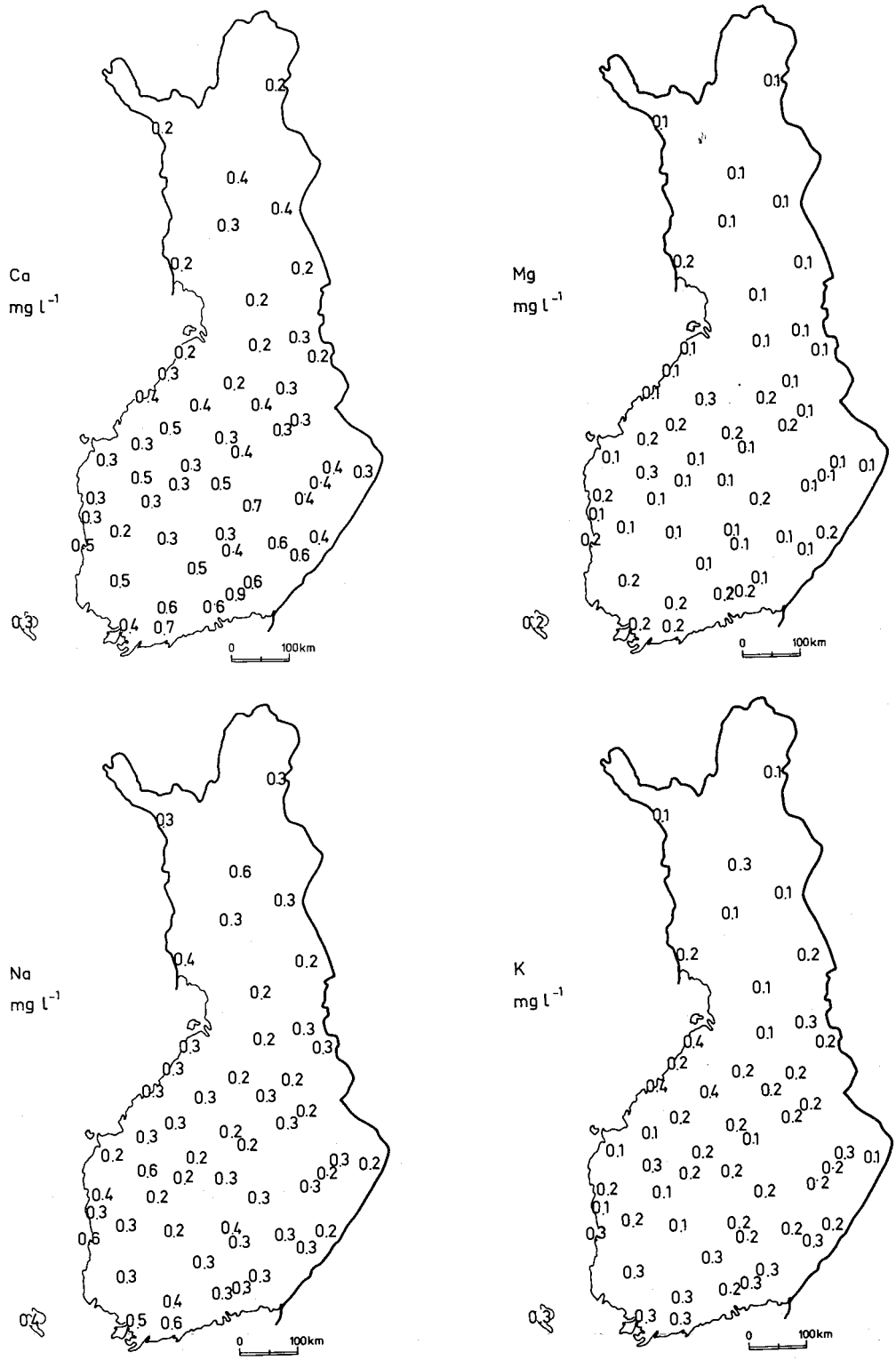

Fig. 6. Mean calcium, magnesium, sodium and potassium concentrations of snowpack in 1976–1984 at the observation stations of National Board of Waters.

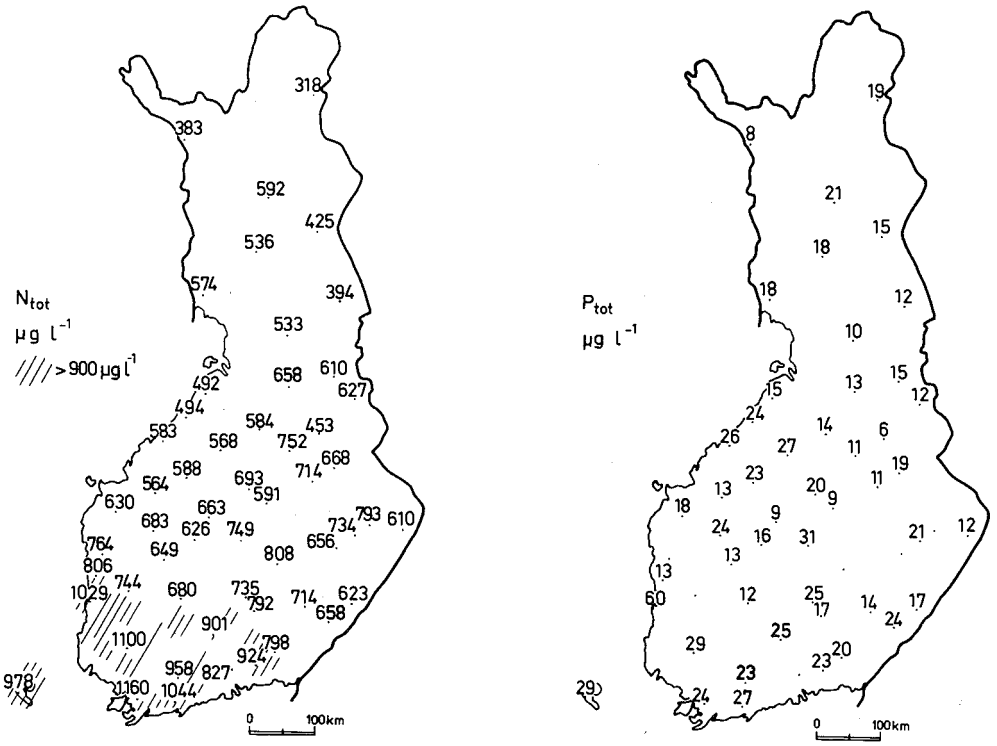

Fig. 7. Mean total nitrogen and total phosphorus concentrations of snowpack during the years 1976–1984 at the observation stations of National Board of Waters.

anomalous regions were detected on the basis of these winter measurements (Fig. 7).

3.14 Chloride and sulfate

The proximity of the sea affects the deposition of both chloride and sulfate. According to the results of rainwater investigations, chloride concentrations in Finland are higher in coastal areas than elsewhere. In northern Finland the Arctic Sea also affects the chloride concentration of rainwater (Järvinen and Haapala 1980).

The mean *chloride* concentrations in snow during the period of this investigation varied at different observation sites between 0.2 and 3.3 mg l^{-1}. The mean for the whole country was 0.8 mg l^{-1}, corresponding to an average monthly deposition of chloride of 20 mg m^{-2}. The chloride concentrations of snow were somewhat higher in the coastal zone than in the remainder of the country (Fig. 8).

Deposition of sulfate was markedly episodic even over short periods of time due to climatic variations. Sulfate deposition also showed a seasonal dependence, winter concentrations being in most cases lower than the corresponding summer figures despite the fact that the use of fossil fuels is greater in winter than in summer (Nordlund 1982). The sulfate concentrations in snow has been found almost 50 % lower than those measured in rainwater (e.g. Barry et al. 1984). These differences were mainly due to the greater solubility of atmospheric sulfur in rainwater than in snow. The sulfur present in the snow cover is in fact mainly the result of dry deposition (Pierson and Taylor 1981).

The snow samples analysed for *sulfate* (n = 277) contained between 0.1 and 7.7 mg l^{-1} (mean 2.2 mg l^{-1}). This corresponds to a monthly deposition of sulfate of about 61 mg m^{-2}.

Clear regional variations were observed in the sulfate concentrations of snow. The level of concentrations was about 3—4 times higher in southern Finland than in the north of the country. The high level of sulfates in the south was obviously due not only to domestic emissions but also to long-distance transportation from other countries. The proportion of the latter fraction has been estimated in different investigations as 50—70

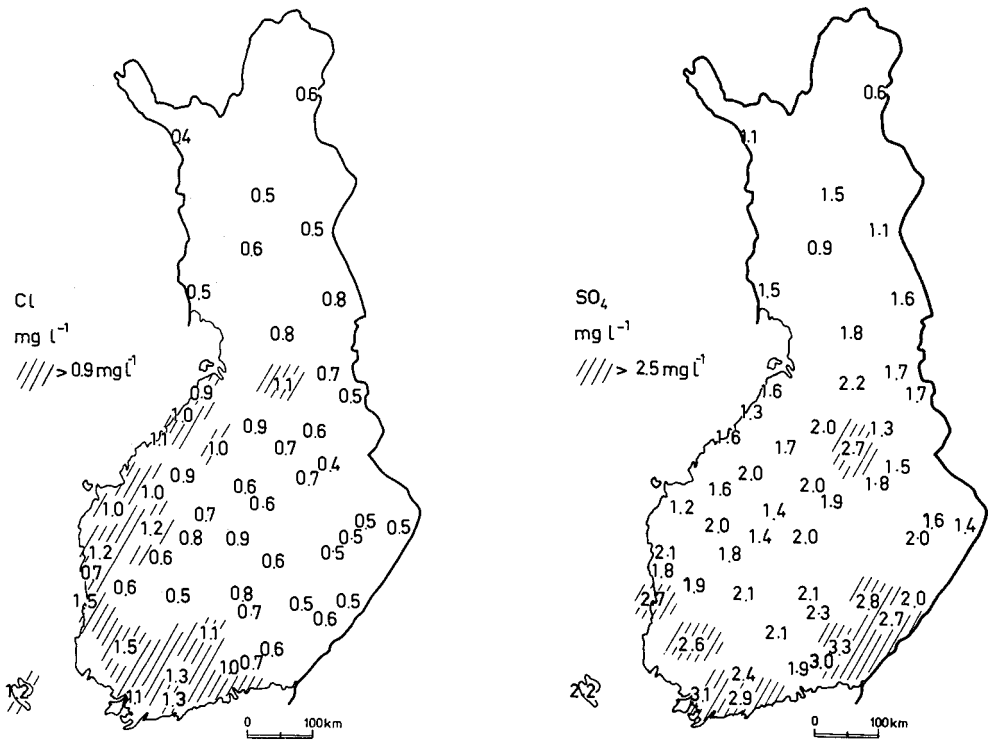

Fig. 8. Mean chloride and sulfate concentrations of snowpack during the period 1976—1984 at the observation stations of National Board of Waters.

% of the total sulfate loading (Fig. 8).

The relationship between the mean concentrations of the group of anions investigated in snow with respect to total phosphorus was:

$$P_{tot} < 41\ N_{tot} < 44\ Cl < 122\ SO_4 \qquad (4)$$

3.15 Heavy metals and aluminium

Many investigations have been published in recent years concerning the heavy metal concentrations occurring in the environment and their effects on various biological processes. Most of the heavy metals are known as environmental pollutants with a direct deleterious effect on humans. These metals accumulate in the body tissues and are not excreted by metabolic processes.

The relative hazard index of a metal is obtained by dividing the ratio of technological emissions to natural flux by the relative toxicity of the metal (Harris and Hohenemser 1978). According to the environmental hazard index the most dangerous heavy metal is mercury, with an index value of 40—1600. The other metals received values as follows: cadmium 13, copper 9, lead 7 and zinc 4.6.

Although heavy metals are generally regarded as environmental pollutants, they are in fact normal components of natural biological cycles and many of them are actually necessary for life. Heavy metals are released from the bedrock by several natural processes, e.g. by weathering, evaporation and erosion as well as a result of volcanic activity.

The metals released from bedrock are eventually distributed between the various natural cycles of the elements into atmoshpere, biosphere, hydrosphere and pedosphere. During recent decades human activities have slowly altered the natural movement of materials and increased the rate of accumulation of metals in the spheres.

Most trace elements occur adhered to solid particles in the atmosphere. The evapotranspiration of vegetation is emitting trace elements in the form of metallo-organic compounds as aetheric vapours. Heavy metals reach the environment mainly via the atmosphere as aerosols, having a particle size of 0.1—2.0 μm. Metal particles may remain airborne for several weeks and therefore become distributed over areas far from their original source (Semb 1978).

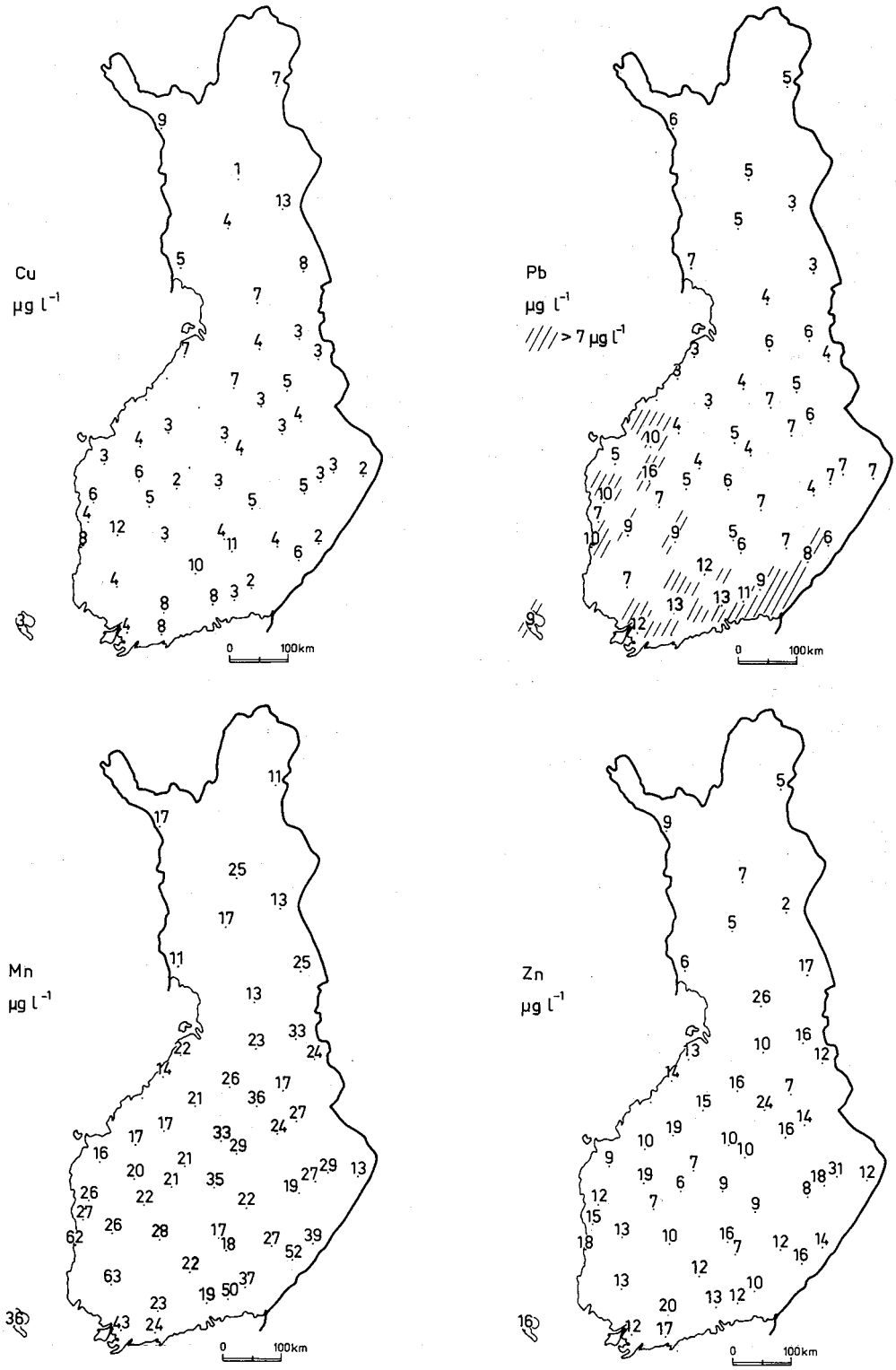

Fig. 9. Mean copper, lead, manganese and zinc concentrations in snowpack, during the years 1976–1984 at the observation stations of National Board of Waters.

Heavy metals emitted from high-temperature processes generally originate as metal vapour and are probably first converted to oxides or carbonates (Semb 1978). Particles larger than 2—3 μm are formed primarily by mechanical processes such as erosion of soil, grinding etc.

The mean background concentrations of copper, lead, manganese and zinc measured in snow in this study were usually low and regional variation was slight (Fig. 9). In the case of *copper* the level of concentrations was slightly higher in northern Finland than in the south of the country. The measured concentrations were between < 1 and 58 μg l^{-1} (mean 6 μg l^{-1} and median 4 μg l^{-1}).

Lead concentrations of snow were markedly higher in the southern than in the northern part of the country, with an overall range of < 1—49 μg l^{-1} (mean 9 μg l^{-1} and median 6 μg l^{-1}). The major factor affecting lead concentrations and their regional variation in Finland is the density of road traffic (Salmi 1969). Lead is principally a pollutant originating from traffic. It reaches the environment mainly in the form of lead halogenides in car exhaust fumes. In addition, mining and lead-utilizing industry release considerable amounts of lead (Soveri 1977). The global lead content of soil has been estimated to be increasing by about 1 ‰ annually as a result of deposition from the air (Ravera 1974).

Manganese concentrations measured in this work were between < 1 and 120 μg l^{-1} (mean 25 μg l^{-1} and median 20 μg l^{-1}). Regional variations in concentration were also recorded in the case of this metal, the concentrations being higher in the south than in the north of the country.

The mean and median values of metal concentrations in snow exhibited a certain degree of discrepancy. This was due to the great difference between extreme values and also partly to lowering of the detection limits during the period of the study. Clearly erroneous results were excluded from the data and median values were used instead of means in the calculations (Table 5).

The *aluminium* concentrations measured were between 20 and 54 μg l^{-1} (mean 30 μg l^{-1} and median 26 μg l^{-1}). Aluminium analyses of snow were carried out only at six observation sites in the water districts of Oulu and Kainuu. The results provide only an estimate of the general level of concentrations and cannot therefore be compared directly with the remained of the data.

The relationships between the concentrations of heavy metals in snow were:

$$Cu < 1.5\ Pb < 2.5.\ Zn < 5\ Mn\ (< 6\ Al) \qquad (5)$$

and the corresponding relationships calculated for the depositions were:

Table 5. Statistical data on the concentrations of copper, lead, manganese and zinc in snow and their mean annual deposition values estimated from the mean and median concentrations during the years 1976—1981.

Parameter	n	Concentration in snowpack (μg l^{-1})				Monthly deposition (mg m^{-2})	
		min	max	mean	median	mean	median
Cu	262	< 1	58	6	4	2	1
Pb	278	< 1	49	9	6	2	2
Mn	266	< 1	120	25	20	10	8
Zn	266	< 1	82	15	10	5	3

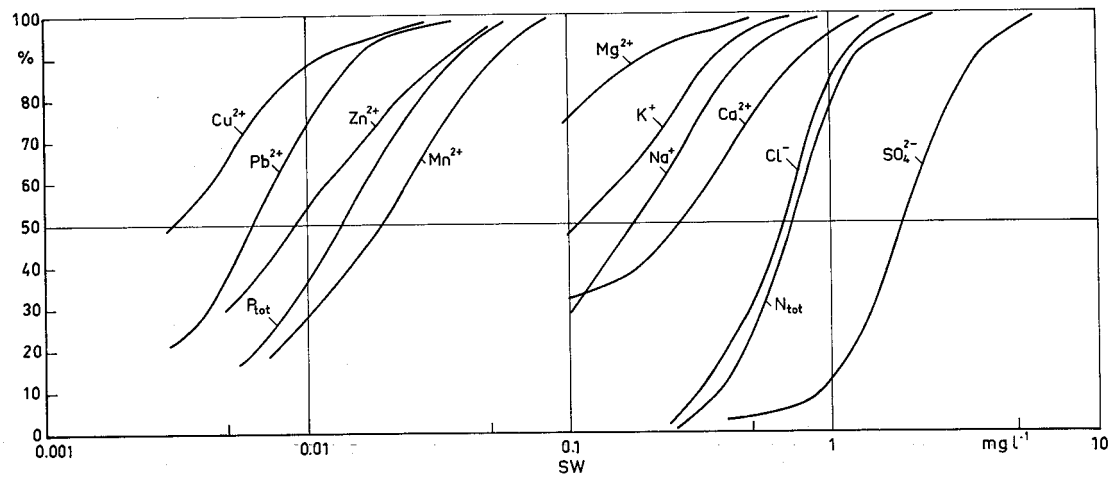

Fig. 10. Cumulative distribution of concentration for various constituents of snowpack at groundwater station during the years 1976–1981.

$$Cu < 2\,Pb < 3\,Zn < 8\,Mn < (10\,Al) \quad (6)$$

The relationships between the substance concentrations of snow and the corresponding deposition values differ from each other mainly due to regional differences in the water equivalent of snow.

Cumulative distribution of concentration for various constituents of snow at groundwater stations during the years 1976—1981 are given in Fig. 10. The relationships between the mean concentrations of cations and anions of whole data were:

$$SO_4 > N_{tot} \approx Cl > Ca > Na > K > Mg > Mn > P_{tot} > Zn > Pb > Cu$$

3.2 Concentrations and deposition patterns

3.21 Concentrations

The chemical characteristics of snow, pH, electrical conductivity and elemental concentrations are presented in Table 6. The interdependences of the constituents in snow were examined statistically by calculation of intercorrelations (Table 7). The statistical significance of the regression analysis is described using the following symbols:

*** = Correlation coefficients are significant at the level of 99.9 %
** = Correlation coefficients are significant at the level of 99 %
* = Correlation coefficients are significant at the level of 95 %

The following regression functions were calculated for the pairs of data having the highest degrees and significance levels of correlation:

$$\gamma_{25} = 0.6 \cdot SO_4 + 1.0 \qquad r = 0.70^{***} \quad (7)$$

$$\gamma_{25} = 0.002 \cdot N_{tot} + 0.9 \qquad r = 0.62^{***} \quad (8)$$

$$Na = 0.2 \cdot Cl + 0.1 \qquad r = 0.53^{***} \quad (9)$$

$$SO_4 = 0.002 \cdot N_{tot} + 0.4 \qquad r = 0.68^{***} \quad (10)$$

$$K = 0.7 \cdot Mg + 0.1 \qquad r = 0.52^{***} \quad (11)$$

$$Pb = 0.3 \cdot Zn + 4.2 \qquad r = 0.55^{***} \quad (12)$$

Table 6. Snow analysis results at the groundwater stations during late winter seasons 1975/1976—1980/1981 (see list of symbols).

Parameter	Unit	n	min	max	mean	median	S	$S_{\bar{x}}$	$S/\bar{x}$
pH		286	3.7	6.2	4.7	4.6	0.4	0.02	0.08
γ_{25}	mS m^{-1}	291	0.6	8.9	2.2	2.1	0.9	0.05	0.42
SO_4	mg l^{-1}	277	0.1	7.7	2.2	1.9	1.2	—	0.53
Cl	mg l^{-1}	283	0.1	3.3	0.8	0.7	0.5	0.03	0.57
Na	mg l^{-1}	281	0.1	1.7	0.3	0.2	0.2	0.01	0.75
K	mg l^{-1}	281	0.1	1.9	0.2	0.2	0.2	0.01	0.84
Ca	mg l^{-1}	284	0.1	2.0	0.4	0.3	0.3	0.02	0.83
Mg	mg l^{-1}	283	0.1	1.6	0.1	0.1	0.1	0.01	0.89
N_{tot}	μg l^{-1}	277	200	1877	736	680	322	19	0.43
P_{tot}	μg l^{-1}	275	<1	84	18	13	14	1	0.79
Cu	μg l^{-1}	262	<1	58	6	4	7	0.4	1.27
Mn	μg l^{-1}	266	<1	120	24	20	19	1.2	0.79
Pb	μg l^{-1}	278	<1	49	8	6	8	0.5	0.90
Zn	μg l^{-1}	266	<1	82	15	10	15	0.9	1.01

Table 7. Correlation coefficients between elements in snowpack during the period 1976—1981.

	pH	γ_{25}	P_{tot}	SO_4	Cl	Na	K	Ca	Mg	N_{tot}	Cu	Mn	Pb	Zn
pH	1.00													
γ_{25}	−0.56***	1.00												
P_{tot}	0.17**	0.04	1.00											
SO_4	−0.28***	0.70***	0.26***	1.00										
Cl	0.27***	0.17**	0.32***	0.30***	1.00									
Na	0.11	0.29***	0.28***	0.30***	0.53***	1.00								
K	0.14*	0.17**	0.47***	0.28***	0.35***	0.38***	1.00							
Ca	0.06	0.23***	0.22**	0.43***	0.21***	0.28***	0.34***	1.00						
Mg	0.18**	0.01	0.13*	0.15*	0.25***	0.20**	0.52***	0.25***	1.00					
N_{tot}	−0.30***	0.62***	0.22***	0.68***	0.20**	0.30***	0.22***	0.25***	0.07	1.00				
Cu	0.07	0.18**	0.04	0.18**	0.25***	0.24***	0.18**	0.25***	0.10	0.15*	1.00			
Mn	−0.02	0.08	0.28***	0.16*	0.18**	0.26***	0.29***	0.29***	0.05	0.07	0.07	1.00		
Pb	−0.07	0.27***	0.16**	0.28***	0.24***	0.35***	0.21***	0.28***	0.06	0.35***	0.47***	0.14*	1.00	
Zn	−0.01	−0.07	−0.16*	0.13*	0.16*	0.30***	0.21***	0.25***	0.04	0.11	0.48***	0.22***	0.55***	1.00

Table 8. Correlation coefficients of different properties of snowpack in the areas of Water Districts.

Water district	γ_{25}/SO_4	γ_{25}/N_{tot}	Na/Cl	SO_4/N_{tot}	K/Mg	Pb/Zn	pH/γ_{25}	Cu/Zn	Mn/Zn	Cu/Pb
Helsinki	0.92***	0.61**	0.52**	0.73***	0.08	0.87***	0.55**	0.79***	0.10	0.89***
Turku	0.90***	0.87***	0.07	0.83***	0.55**	0.37	0.70***	0.58**	0.42*	0.37
Tampere	0.78***	0.80***	0.51*	0.74***	0.72***	0.40	0.82***	0.88***	0.71***	0.54*
Kymi	0.77**	0.96***	0.28	0.76**	0.39	0.25	0.57*	0.30	0.01	0.55
Mikkeli	0.45*	0.37	0.80***	0.48*	0.40	0.16	0.72***	0.56*	0.38	0.14
Kuopio	0.67***	0.30	0.38	0.39	0.08	0.34	0.78***	0.53*	0.06	0.35
Pohj.Karjala	0.85***	0.88***	0.85***	0.85***	0.176	0.48*	0.86***	0.54*	0.30	0.24
Vaasa	0.87***	0.64***	0.68***	0.87***	0.60**	0.77***	0.50*	0.72***	0.49*	0.44*
Keski-Suomi	0.49*	0.55*	0.25	0.42	0.34	0.24	0.50*	0.54*	0.11	0.14
Kokkola	0.46	0.57**	0.32	0.55*	0.94***	0.19	0.64**	0.69**	0.52*	0.37
Oulu	0.71**	0.74***	0.90***	0.55*	0.33	0.78*	0.63**	0.68*	0.39	0.60*
Kainuu	0.38	0.54*	0.22	0.68***	0.07	0.67***	0.38	0.41	0.01	0.70***
Lappi	0.58**	0.55**	0.34	0.43	0.41	0.80***	0.70***	0.86***	0.26	0.89***
Finland	0.70***	0.62***	0.53***	0.68***	0.52***	0.55***	0.56***	0.48***	0.22**	0.47***

$$pH = -0.2 \cdot \gamma_{25} + 5.2 \qquad r = -0.56^{***} \qquad (13)$$

$$Cu = 0.2 \cdot Zn + 2.4 \qquad r = 0.48^{***} \qquad (14)$$

$$Cu = 0.3 \cdot Pb + 2.2 \qquad r = 0.47^{***} \qquad (15)$$

The correlation coefficients describe the reciprocal deposition-based relationship between the values of the data pairs in snow. For example sulfate and total nitrogen concentrations have the greatest effect on the electrical conductivity (γ_{25}) of snow. Human activities, long distance transport of air pollutants and in coastal areas the proximity of the sea have the greatest effects on the electrolyte contents of deposition and of snow in the conditions prevailing in Finland. The effect of regional factors on the quality of snow is examined by comparison of correlations in the 13 Water Districts in Table 8 (see also Figs. 5—9).

The correlation between sulfate concentration and electrical conductivity was strongest ($r = 0.92^{***}$) in the area of the most densely populated Helsinki Water District. The range of correlations in the different Water Districts varied considerably, depending on e.g. population density and the level of industrialization. Thus in the sparsely populated, non-industrialized areas in Kainuu the correlation coefficient for this pair of data was only 0.38, where obviously other factors than sulfates affected the conductivity.

The correlations between the different heavy metal concentrations were very clear in the sparsely populated areas. Deposition of heavy metals in these areas corresponds most closely to the natural balanced state, in which the effect of human activities is only slight. For example the correlation between copper and lead was ($r = 0.70^{***}$) in Kainuu and ($r = 0.89^{***}$) in Lapland. Again in Lapland the correlation between copper and zinc was ($r = 0.86^{***}$), and between lead and zinc ($r = 0.80^{***}$).

Some of the correlations between metals were significant even in the more densely populated areas. In the Helsinki Water District the correlation between lead and zinc was ($r = 0.87^{***}$), and between lead and copper ($r = 0.89^{***}$).

The effect of the proximity of the sea on the materials balance in snow was clearest in the Oulu Water District, where the correlation between sodium and chloride was as high as ($r = 0.90^{***}$). The late freezing of the sea apparently also affects the elemental concentration in snow.

3.22 Deposition patterns

The depositions of different materials and their mean and deviation values for the winter seasons 1975/1976 . . . 1980—1981 have been calculated in Table 9 according to equation (1).

The extreme values of deposition varied considerably in many cases, due to regional differences in loading. The reciprocal relationships between the deposition values were investigated for the whole country in a similar manner to the snow analysis results.

The regional comparison was also carried out by pairs of parameters in the different Water Districts. The results are presented in Tables 10 and 11.

The material concentrations of the snow cover reflect the primary situation from which the substances in both watercourses and groundwater have their origin. The element concentrations of snow also reveal atmospheric loading. Regional and local loading have been estimated as deposition

Table 9. Mean and deviation values of the monthly deposition to the snowcover during the winter seasons 1975/1976 . . . 1980/1981.

Parameter	Unit	n	min	max	mean	median	S	$S_{\bar{x}}$	$S/\bar{x}$
P_{tot}	mg m^{-2}	276	0.1	3.3	0.5	0.4	0.5	0.03	0.91
SO_4	mg m^{-2}	278	1.0	295.3	59.4	53.0	35.6	2.14	0.60
Cl	mg m^{-2}	283	1.4	98.4	21.2	17.6	13.3	0.79	0.63
Na	mg m^{-2}	282	0.2	42.9	7.6	6.1	6.1	0.36	0.80
K	mg m^{-2}	281	0.2	46.3	6.2	4.5	5.4	0.32	0.87
Ca	mg m^{-2}	283	0.5	51.3	10.7	8.6	9.1	0.54	0.85
Mg	mg m^{-2}	285	0.2	39.0	4.1	3.2	4.0	0.24	0.97
N_{tot}	mg m^{-2}	276	0.8	62.5	20.1	18.1	10.6	0.64	0.57
Cu	mg m^{-2}	268	<0.1	1.4	0.2	0.1	0.2	0.01	1.09
Mn	mg m^{-2}	266	<0.1	3.2	0.7	0.5	0.6	0.04	0.86
Pb	mg m^{-2}	278	<0.1	1.2	0.2	0.2	0.2	0.01	0.85
Zn	mg m^{-2}	271	<0.1	3.5	0.4	0.3	0.5	0.02	1.04

Table 10. Correlation coefficients between elements in snow deposition during the period 1976—1981.

	P_{tot}	SO_4	Cl	Na	K	Ca	Mg	N_{tot}	Cu	Mn	Pb	Zn
P_{tot}	1.00											
SO_4	0.22***	1.00										
Cl	0.31***	0.40***	1.00									
Na	0.29***	0.31***	0.48***	1.00								
K	0.40***	0.25***	0.38***	0.34***	1.00							
Ca	0.34***	0.41***	0.20**	0.29***	0.34***	1.00						
Mg	0.13*	0.19**	0.37***	0.18**	0.38***	0.20**	1.00					
N_{tot}	0.27***	0.71***	0.28***	0.35***	0.22**	0.36***	0.11	1.00				
Cu	0.01	0.13*	0.06	0.10	0.07	0.07	0.02	0.15*	1.00			
Mn	0.29***	0.27***	0.21**	0.20**	0.29***	0.29***	0.15*	0.29***	0.06	1.00		
Pb	0.09	0.26***	0.19**	0.38***	0.15*	0.29***	0.05	0.24***	0.26***	0.11	1.00	
Zn	0.08	0.16*	0.17**	0.30***	0.14*	0.23***	0.06	0.16*	0.16*	0.19*	0.48***	1.00

Table 11. Correlation coefficients between deposition results by Water District.

Water districts	P_{tot}/Na	SO_4/N_{tot}	Cl/Na	Cl/Mg	Na/K	Na/Ca	K/Ca	K/Mg	Ca/Mg	Cu/Zn	Cu/Pb	Mn/Zn	Pb/Zn
Helsinki	0.03	0.71***	0.60**	0.28	0.54**	0.16	0.25	0.01	0.27	0.70***	0.90***	0.18	0.83***
Turku	0.26	0.71***	0.56**	0.51*	0.54**	0.46*	0.53**	0.64**	0.38	0.83***	0.73***	0.21	0.73***
Tampere	0.77***	0.78***	0.90***	0.76***	0.67***	0.76***	0.78***	0.75***	0.79***	0.66**	0.04	0.59**	0.36
Kymi	0.05	0.76**	0.10	0.23	0.26	0.41	0.21	0.47*	0.40	0.21	0.33	0.29	0.39
Mikkeli	0.42	0.79***	0.60**	0.01	0.60**	0.36	0.55**	0.16	0.49*	0.50*	0.16	0.36	0.33
Kuopio	0.03	0.26	0.12	0.73***	0.35	0.26	0.46*	0.11	0.25	0.45	0.01	0.13	0.27
Pohj.Karjala	0.22	0.73***	0.72***	0.22	0.06	0.33	0.39	0.43*	0.39	0.36	0.07	0.21	0.24
Vaasa	0.76***	0.92***	0.64***	0.74***	0.80***	0.72***	0.90***	0.55**	0.43*	0.63**	0.48*	0.55**	0.81
Keski-Suomi	0.28	0.67**	0.66**	0.54*	0.42*	0.29	0.38	0.46*	0.62**	0.51*	0.41	0.12	0.35
Kokkola	0.23	0.12	0.13	0.05	0.10	0.30	0.65**	0.91***	0.54*	0.15	0.21	0.50**	0.58**
Oulu	0.08	0.65***	0.44	0.56	0.21	0.29	0.25	0.09	0.15	0.26	0.20	0.10	0.80***
Kainuu	0.06	0.83***	0.23	0.27	0.35	0.01	0.08	0.05	0.73	0.44	0.73***	0.12	0.64**
Lappi	0.38	0.45*	0.17	0.06	0.64**	0.11	0.49*	0.01	0.15	0.76***	0.81***	0.15	0.70***
Finland	0.29***	0.71***	0.48***	0.37***	0.34***	0.31***	0.34***	0.38***	0.20**	0.10	0.16**	0.40***	0.36**

values, in which both the amount of snow and the time of deposition have been taken into account.

Of the depositions for the whole country (Table 10) the best intercorrelations were between the depositions of sulfate and total nitrogen (r = 0.71***), sodium and chloride (r = 0.48***) and sulfate and chloride (r = 0.40***).

The correlation coefficients between the deposition of different elements were greater for smaller regions than for the whole country. This was at least partly due to the fact that regional factors affecting deposition (industry, population density) have a significant effect on the internal relations of materials in snow. For example in the Helsinki Water District the best intercorrelations were recorded between sulfate and total nitrogen (r = 0.71***), copper and lead (r = 0.90***) and lead and zinc (r = 0.83***), all of which are emitted in the production of energy from fossil fuels (Table 11).

4. INFILTRATION OF MELTWATER AND ITS CHEMICAL COMPOSITION

4.1 Infiltration in different soil types

Snow is a porous material and is in this sense comparable with soil. The flow of water through both snow and soil largely conforms to Darcy's classical equation assuming that the flow rates remain rather low.

The permeability of liquid through soil and snow layers depends on the degree of saturation of the soil or snow matrix. The vertical flow is driven almost entirely by gravitational forces. The vertical flux of water through the snowpack can be approximated e.g. according to the equation of Bengtsson (1982) as:

$$v = k_D \Theta_*^a, \tag{16}$$

where

v = vertical flux of water
k_D = saturated hydraulic conductivity
Θ_* = effective water content, defined as

$$\Theta_* = \frac{\Theta - \Theta_i}{n - \Theta_i} \varnothing (\Theta - \Theta_i), \tag{17}$$

where

a = empirical coefficient
n = porosity of the snow
$\varnothing$ = unit step function
Θ = liquid content of the snow
Θ_i = the irreducible liquid content

Meltwater on the surface of the ground infiltrates into the soil first by filling the pore spaces and then by moving downwards under the influence of gravity.

Both the mean size of individual voids and their total volume are therefore of importance for infiltration, as is the degree to which the pores are interconnected.

Infiltration of meltwater begins when the ground is still frozen (Lemmelä 1972). Freezing of the ground does not prevent snowmelt infiltration, although it does to some extent slow down the process. An example of a frozen moraine soil in which changes in water content indicate infiltration in the soil is presented in Table 12. Increase in soil moisture in the frozen layers is also partly due to the thermal gradient, as a result of which moisture condenses on the soil frost penetration depth in conjunction with heat transfer.

The degree of saturation of soilwater storage is highest during the spring flood. The amount of infiltration depends on the hydraulic conductivity of the soil and the adsorption properties of both the water and mineral surfaces. If the amount of infiltrating water exceeds the saturation capacity of the soil the excess water is lost as surface or sub-

Table 12. Soil moisture (vol. %) and soil frost depth (broken line) at the Karkkila experimental station in 1971 and 1972 (Soveri and Varjo 1977).

Depth cm	Date of measurement							
	8.10.	5.11.	3.12.	7.2.	10.3.	3.5.	30.5.	28.6.
00								
10								
20	32.4	33.7	33.6	36.1	36.3	47.4	33.1	24.9
30	34.3	36.0	34.3	34.8	35.0	44.6	38.5	31.6
40	34.5	35.1	43.1	33.1	34.3	41.9	37.9	31.7
50	38.7	39.1	40.1	35.6	36.1	37.9	37.9	35.8
60	41.4	40.4	40.5	39.0	38.9	40.9	41.4	39.2
70	42.0	40.7	40.9	40.1	40.5	41.6	41.6	39.7
80	41.6	41.4	41.2	40.2	41.0	43.1	40.5	39.2

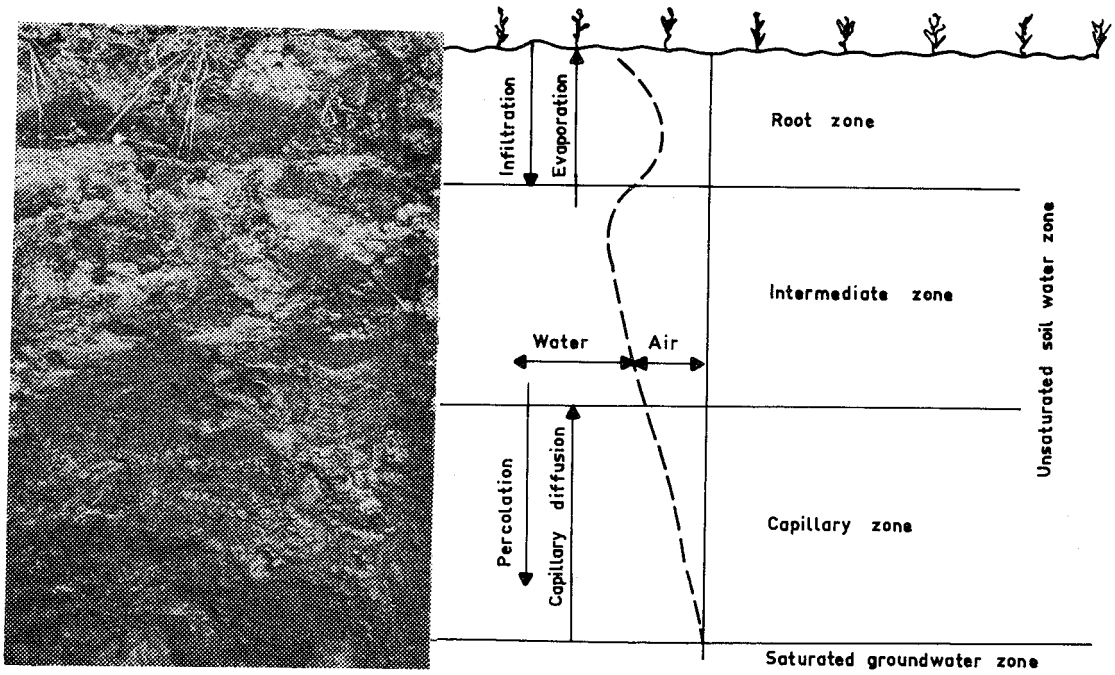

Fig. 11. Scheme of the water relations of soil in unsaturated and saturated zones.

surface runoff. During the snowmelt season evaporation is of only minor significance and the water requirement of vegetation is slight.

The scheme of soil water relations between soil surface and groundwater is presented in Fig. 11.

When the infiltration due to gravitational forces ceases the soil moisture content attains the field capacity value and the surface tension of the soil water (pF) varies according to the soil type between 1.7 and 2.3 (Vesihallitus 1976). The moisture balance of the soil, i.e. the adsorption of soil water, is then affected particularly by separate forces such as gravitation, matrix and osmosis potentials (e.g. Kristensen 1970).

In fine grained soils the dry crust layer of top soil is not appreciably permeable to meltwater, but to some extent retains it. In clay and silt soils the movement of soil water takes place mainly by capillary action from the groundwater to the soil surface, from where it is removed by evaporation (Soveri 1970).

The amount of water infiltrating from meltwater (IW) and the total annual infiltration (I_a) were measured by lysimeter. The basis for calculation of infiltration was the maximum water equivalent of snow, to which was added the amount of precipitation occurring during the thaw season. This total is referred to below as meltwater (SW).

The infiltration due to meltwater was estimated from a cumulative infiltration curve by drawing a tangent to the steepest part of the curve. The method used for estimation of total infiltration is presented in Fig. 12.

The meltwater moving freely under the influence of gravity was considered as finished when the tangent departed from the infiltration curve (see Fig. 12). The water partly adsorbed on the soil particles by adhesion and capillarity filtered through more slowly. In conjunction with the latter slow filtering the capillary water immobilized during the formation of the frozen soil layer is released. This water corresponds approximately to the amount of water released from coarse-grained soils as later infiltration.

The infiltration resulting directly from melting was always finished before the attainment of the maximum height of ground water. There is a certain time lag between infiltration and the formation of groundwater. The duration of this time lag is depended on the hydraulic conductivity of the soil and the infiltration distance.

In the example given in Fig. 12 the dependence of groundwater formation on infiltration is examined in a sandy soil at the Kuuksenvaara groundwater station in northern Karelia. The infiltration resulting from the spring thaw in 1979 was 68 mm,

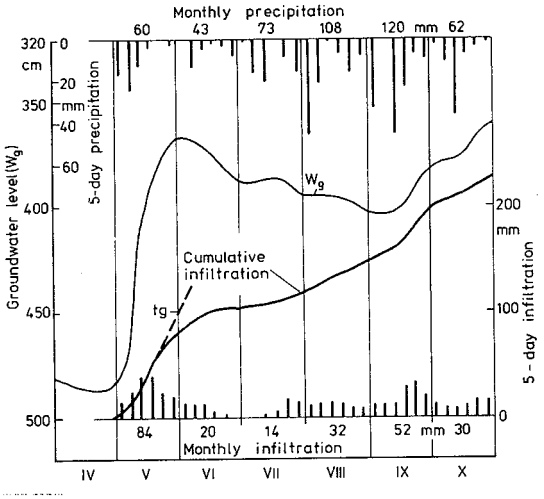

Fig. 12. The effect of meltwater and precipitation on infiltration and the formation of groundwater at the Kuuksenvaara (25) groundwater station in 1979.

corresponding to 52 % of the total meltwater (130 mm). It is 29 % of the total annual infiltration (232 mm), which of the uncorrected annual precipitation of 595 mm is 39 %. The latter figure corresponds to the average formation of groundwater from precipitation in the soil type concerned. The true precipitation figures are, due to systematic errors, on average 15—22 % greater than those presented in this study. These errors in the collecting vessels are mainly caused by aerodynamic factors and by so-called droplet adhesion. The errors are smaller in the south of Finland than in the north (Ekholm and Solantie 1985).

In the summer months (June, July and August) of 1979 a total of 66 mm of groundwater was formed from the rainfall of 224 mm. During this time the level of the groundwater fell continuously because the amount of infiltration was less than the amount of excaping groundwater. Reduction in the groundwater level during the summer months is a common occurrence. It does not necessarily mean that groundwater is not being formed, but only that discharge of the groundwater reserve is taking place faster than replenishment. In the example in Fig. 12 on infiltration into the lysimeter occurred whatsoever during a 17-day period in June-July.

The significance of evapotranspiration is often considerable during the summer season. Estimated on the basis of the water balance at the lysimeter installed at the Kuuksenvaara site, evaporation and surface runoff together accounted for 158 mm or 71 % of the summer season precipitation (244 mm).

Formation of groundwater was rapid during September and October of 1979. Of the total precipitation of 182 mm, infiltration was 82 mm, leaving the share of evaporation and surface runoff as 100 mm or 55 % of the precipitation. The rapid formation of groundwater was due partly to the high degree of saturation of the soil, which in turn resulted from an unusually rainy August.

The proportion of infiltration of meltwater and total precipitation in sorted and unsorted soils is examined in detail in Fig. 13 and in Tables 13 and 14. A total of 37 observation years and 13 lysimeters is included in the examination.

The proportion of infiltration of meltwater and annual precipitation varied considerably in different years in a given soil type depending on precipitation and its temporal distribution. In sorted soils 23—71 % (mean 41 %) of the meltwater filtered through the soil, whereas in unsorted soils the infiltration was 17—64 % (mean 39 %). The proportion of infiltration of the total annual precipitation was in sorted soils 35—88 % (mean 61 %) and in unsorted soils 25—46 % (mean 39 %).

The contribution of meltwater to the total annual groundwater reserve was considerably smaller than was earlier generally believed. In sorted soils the infiltration of meltwater was only 13—44 % (mean 28 %) of the total annual infiltration. In unsorted soils the corresponding figure was 16—36 % (mean 27 %).

The infiltration of spring meltwater is dependent on the depth of the frozen layer and on the degree of moisture saturation of the soil. The massive freezing associated with sandy and gravely soils reduces the infiltration capacity of the soil. The effect of the depth and massiveness of the frozen layer on the permeability of the soil to water varies in different years according to the degree of moisture saturation at the beginning of the freeze, the cumulative total of frost, the depth of the snow cover and the date of initiation of the permanent snow cover (Soveri and Varjo 1977).

In unsorted soil types frozen ground often occurs as rather irregular zones, which have a greater permeability to water than that of the massive layer of frozen ground. This partly explains why relatively more meltwater infiltrates through till soils than in the area of massive freezing in sandsoils.

In Fig. 13 the dependence of infiltration on meltwater and total precipitation in sorted soil-type areas is examined in different soils.

The coefficients of the curves describing the formation of infiltration water indicate almost without exception that infiltration due to the

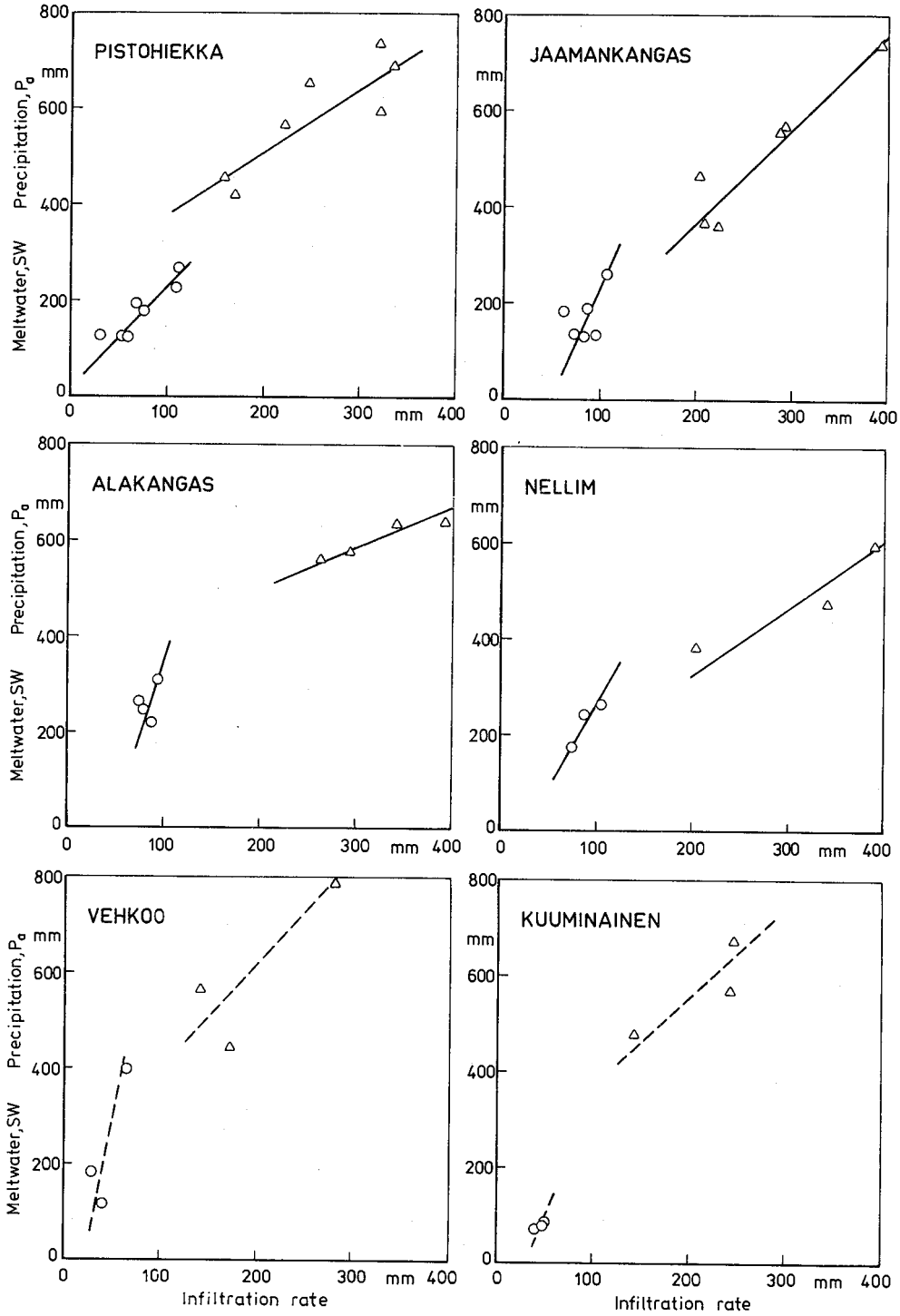

Fig. 13. The proportion of infiltration of meltwater and annual precipitation in sorted soils at the lysimeter fields at Pistohiekka (18), Jaamankangas (26), Alakangas (47) and Nellim (54) and in silt and till soils at Vehkoo (34) and Kuuminainen (8), O = meltwater, Δ = annual precipitation.

Table 13. The proportion of infiltration of meltwater and of total precipitation in sorted and coarse-grained soil types.

Lysimeter station	Year	Soil type %			SW mm	IW mm	IW/SW %	P_a mm	I_a mm	I_a/P_a %	SW/P_a %	IW/I_a %
		Silt	Sand	Gravel								
Pertunmaa	1980	4	52	44	169	49	29	531	335	63	50	15
	1981				255	92	36	739	557	75	35	17
	$\bar{x}$				*212*	*71*	*33*	*635*	*446*	*69*	*48*	*16*
Pistohiekka	1976	4	90	6	124	46	37	411	192	47	30	24
	1977				198	66	33	596	320	54	33	20
	1978				129	30	23	455	157	35	28	19
	1979				173	74	43	691	332	48	25	22
	1980				161	50	31	568	220	39	28	23
	1981				261	110	42	738	320	43	35	34
	1982				223	108	48	654	248	38	34	44
	$\bar{x}$				*181*	*69*	*39*	*587*	*212*	*44*	*31*	*33*
Naakkima	1980	2	88	10	132	54	41	653	306	47	20	18
	1981				239	80	33	679	393	58	35	20
	$\bar{x}$				*186*	*67*	*37*	*666*	*350*	*53*	*28*	*19*
Jaamankangas	1976		~100		136	96	71	378	224	59	36	43
	1977				191	86	45	556	287	52	34	30
	1978				128	84	66	371	208	56	35	40
	1979				184	62	34	463	202	43	40	31
	1980				136	74	54	568	291	51	24	25
	1981				264	108	41	743	393	53	36	27
	$\bar{x}$				*173*	*85*	*49*	*513*	*254*	*52*	*34*	*33*
Jämijärvi	1978		*~80*	*~20*	*140*	*64*	*46*	*542*	*476*	*88*	*26*	*13*
Juutilankangas	1978	*~5*	*~80*	*~15*	*177*	*80*	*45*	*425*	*284*	*67*	*42*	*28*
Turtankangas	1978		~80	~20	153	60	39	405	240	59	38	25
	1980				124	70	56	353	200	57	37	
	$\bar{x}$				*139*	*65*	*47*	*379*	*220*	*58*	*37*	*30*
Alakangas	1979	6	85	9	227	86	38	643	393	61	35	22
	1980				259	75	29	576	292	51	45	26
	1981				248	80	32	634	343	54	39	23
	1982				302	92	30	563	261	46	54	35
	$\bar{x}$				*259*	*83*	*32*	*604*	*322*	*53*	*43*	*26*
Nellim	1980				171	75	44	384	201	52	45	42
	1981				248	86	35	597	391	66	42	22
	1982				264	105	40	469	343	68	56	25
	$\bar{x}$				*228*	*83*	*37*	*483*	*303*	*63*	*47*	*27*
	Σ *28*			*min*	*124*	*30*	*23*	*353*	*157*	*35*	*20*	*13*
				max	*264*	*110*	*71*	*743*	*557*	*88*	*56*	*44*
				$\bar{x}$	*188*	*77*	*41*	*511*	*300*	*61*	*36*	*27*

Table 14. The proportion of infiltration of meltwater and of total precipitation in unsorted and fine-grained soil types.

Lysimeter station	Year	Soil type %			SW mm	IW mm	IW/SW %	P_a mm	I_a mm	I_a/P_a %	SW/P_a %	IW/I_a %
		Silt	Sand	Gravel								
Vehkoo	1976	80	10		180	30	17	446	172	39	40	17
	1980				168	40	24	566	142	25	30	28
	1981				399	66	17	802	280	35	50	24
	$\bar{x}$				*249*	*45*	*18*	*604*	*198*	*33*	*41*	*23*
Kuuminainen	1978	~20	~60	~20	78	50	64	477	141	30	16	35
	1979				83	52	63	675	245	36	12	21
	1980				74	40	54	566	246	43	13	16
	$\bar{x}$				*78*	*47*	*61*	*573*	*211*	*36*	*14*	*22*
Jakokoski	1982	*~20*	*~60*	*~20*	*225*	*88*	*39*	*543*	*247*	*45*	*41*	*36*
Kullisuo	1981	26	57	17	266	88	33	617	245	40	43	36
	1982				288	82	28	600	278	46	48	29
	$\bar{x}$				*277*	*85*	*31*	*609*	*262*	*43*	*45*	*32*
	Σ *9*			*min*	*47*	*20*	*17*	*446*	*141*	*25*	*12*	*16*
				max	*399*	*88*	*64*	*802*	*280*	*46*	*50*	*36*
				$\bar{x}$	*257*	*65*	*37*	*582*	*230*	*38*	*33*	*27*

spring snowmelt is relatively less than the total infiltration due to annual precipitation. Precipitation and its temporal distribution is the most important factor effecting infiltration and the formation of groundwater.

At the Jaamankangas and Kuuminainen lysimeter fields the annual variation in total infiltration was also examined in sand and till soil types (see 4.11).

4.11 Infiltration in the unsaturated zone

The temporal distribution and duration of infiltration vary in different years (Fig. 14). Summer rainfall may have a great effect on total infiltration. Rainfall in itself is not sufficient to explain the infiltration, the temporal distribution of rainfall is also important. Changes in soil moisture regulate the relationship between rainfall and the formation of groundwater. The changes in the soil water reserve may vary according to the soil type and the depth of unsaturated zone of the soil about between 50 and 200 mm. Thus in certain cases even heavy rainfall may be totally adsorbed into the soil water zone, from where the water may be evaporated by capillary action without any contact with the groundwater (Soveri 1972).

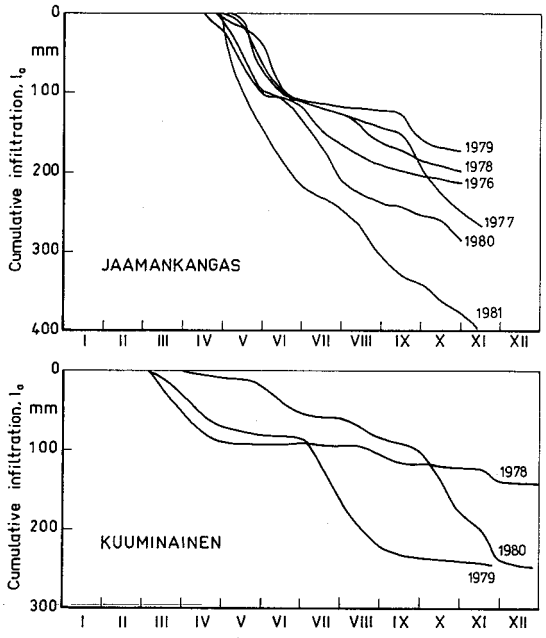

Fig. 14. Annual infiltration in sandy soil at the Jaamankangas and in till soil at the Kuuminainen lysimeter fields during the period 1976—1981.

Total infiltration and its annual variation are largely affected by the following factors:

— the thickness and water retention capacity of the organic surface
— the degree of saturation and water retention capacity of the unsaturated mineral soil
— the particle size and mineral composition and structure of the soil
— the amount and temporal distribution of precipitation
— evapotranspiration by vegetation

The correlation between infiltration and the recharge of groundwater was examined in closer detail at the Jaamankangas groundwater station during climatically different years (Fig. 15). The year 1979 was drier and snow equivalent lower than the mean, whereas 1981 was considerably wetter and summer rainfall had an unusually great effect on the recharge of groundwater (see Table 2).

The area of Jaamankangas is a large, unified groundwater area with considerable importance from the point of view of water supply. Geologically the area is a delta formation adjoining to the Salpausselkä range. Within this formation the surface of the groundwater is at an average depth of nine metres. The time lag between precipitation and groundwater recharge in the area is about 30—45 days.

Fig. 15 illustrates the significance of melting and summer rainfall in the formation of groundwater during different precipitation years.

The long-term (1931—1960) uncorrected mean of total precipitation during the period May-October at the meteorological station at Kuopio Airport was 369 mm. Precipitation during the same period (May-October) in 1979 was 320 mm but in 1981 it was 500 mm (Finnish Meteorological Institute, 1979 and 1981).

After the spring thaw of 1979 the groundwater reserve at Jaamankangas did not increase during the period of summer precipitation, although slight infiltration was taking place throughout the period of observation. Not until the onset of the autumn rain did infiltration increase to the extent that replenishment of the groundwater reserve occurred.

In 1981 the water equivalent of snow at the beginning of the snowmelt was high. In addition, rainfall during the period June-August was exceptionally high, 36 % higher than the mean. Furthermore, the rainfall was distributed rather evenly over this 3-month period. Infiltration was also uniformly high during this observation period and thus the groundwater reserve increased continuously.

The proportion of infiltration of the precipitation at Jaamankangas was 41 % in 1979 and 53 % in 1981. During the high — rainfall season the

relative proportion of infiltration was considerably higher than in the drier season, due to the different degree of saturation of the soil in the different years.

The soil water reserve and especially the saturation deficit in the soil regulates the percolation. During dry seasons in sorted soils the saturation deficit of the soil must first be saturated before percolation can occur. With the filling of the saturation deficit the water content of the soil approaches equilibrium with the volume of soil pores. Only when the moisture balance corresponding to the field capacity is exceeded does percolation begin in response to the force of gravity. If the moisture of the soil does not exceed its saturation deficit, part of the moisture remains as interstitial water in the soil pores or is lost by evaporation.

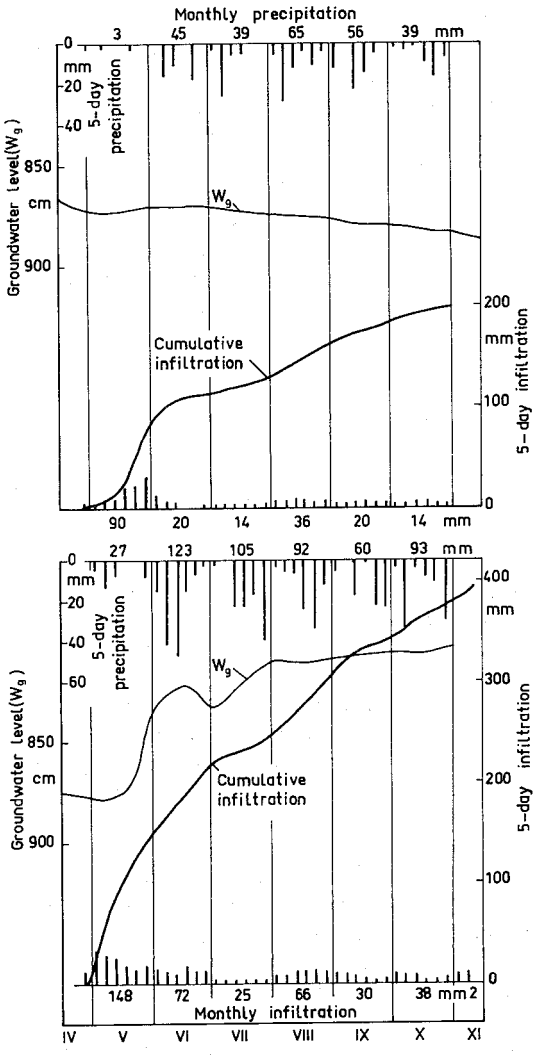

Fig. 15. The effect of meltwater and precipitation on infiltration and the formation of groundwater at the groundwater station at Jaamankangas, during a rather dry year (May-October), 1979 (upper figure) and during a wetter than average season (May-October), 1981 (lower figure).

Seuna (1983) has investigated the role of different regional factors on infiltration by infiltrometer tests. The final filtering of water has best been explained by the percentage of finest soil types and by the thickness of the organic layer. A modification of antecedent precipitation index describing the moisture deficit of the soil was also found to be a significant factor, as was the extent of stratification of the soil.

Mustonen (1963) has investigated the effect of meteorological and regional factors on runoff. He has obtained the following regression equation between spring runoff (y) on the one hand and the water equivalent of snow (x) and spring precipitation (z) on the other:

$$y = 7 + 0.53\,x + 0.98\,z, \qquad (18)$$

where all variables are expressed in mm.

According to Mustonen a rough estimate of the proportion of spring runoff of spring precipitation and the water equivalent of snow was 2/3 in arable land. The remainder evaporates or formes soil water and groundwater. This estimate corresponds rather well with results obtained by infiltration experiments in fine-grained soil types. In silt soil (Vehkoo), which corresponds most closely to the arable land of Mustonen, the mean infiltration was 18 % of the spring meltwater during the years 1976, 1980 and 1981. Calculating indirectly from equation (18) the combined proportion of evaporation and infiltration was 26 % of the spring meltwater.

4.2 Chemical composition of infiltration water

Snow meltwater is the primary agent of weathering and also the solution for the transport of the weathering products. Changes due to acid meltwater already begin in the organic topsoil level and continue in the unsaturated zone. When meltwater penetrates the soil profile and reaches the groundwater surface its acidity usually has decreased, due to buffering processes in the soil. Buffering is affected by several factors, the most important of

which is the concentration of active bases in the soil (Overrein 1972). The exchangeable base cations, mainly Ca^{2+}, play a deciding role in buffering acidification pushes, which are caused by the temporal discoupling of the ion cycle (Ulrich and Pankrath 1983 eds.).

The mobility of different weathering products in soil and in the soil water system may vary considerably. Calcium is mobile to some extent, and sodium is considerably more mobile than potassium, although both occur in almost equal amounts in the primary igneous material (Matthess 1982). The selectivity of cation adsorption, for example, is related to their valency. The mechanism of anion adsorption and exchange is more complex and less well known, especially for polyvalent ions as phosphate (Wiklander 1978).

Many natural biological processes take place in the organic surface layer of the soil and in the root zone. Such processes include extraction of nutrients from soil by plants, formation of humic and fulvic acids, production of carbon dioxide by plants and other organisms, the humification of organic material and ion exchange. These processes influence the various material concentrations in the percolating water and thus also in the groundwater.

As acid meltwater is adsorbed into the soil, it reacts with minerals by exchanging cations. This process tends towards a state of dynamic equilibrium between solid and solution phases by the mechanism of cation exchange. The hydrogen ions in the meltwater are replaced by metal ions from the soil particles, in particular by calcium, but also other metal ions of the soil particles. These reactions continue until dynamic equilibrium is reached.

Percolating water and dominating natural acids dissolve calcium, magnesium and potassium from the surfaces of the soil minerals, and transport the ions to the groundwater. The weathering of cations and their exchange with hydrogen are the main reasons why the pH of the infiltration water and of the groundwater is higher than that of the snow meltwater. According to the results of lysimeter experiments, the pH of meltwater changes by 2 to 3 units when passing through 170 cm of organic and sandy soil (Soveri 1981).

The dissolved carbon dioxide in percolating water is also active in destroying minerals (Stumm and Morgan 1981). If infiltration is rapid, saturation with CO_2 occurs first and weathering takes place when the water reaches the groundwater table. When the infiltration is slow, weathering may already take place in the soil zone to a large degree and the water is continuously fed with CO_2, replacing that which is consumed. It is obvious that the latter type of infiltration will introduce ultimately more carbonates ($HCO_3^- + CO_3^{--}$) and more cations to the water (Jacks 1973b).

The composition of the adsorption complex depends on the relative concentrations in solution and on the relative affinities of different components for the solid phase.

Sorptive bonding on the soil solid phase may be caused by a number of different types of interactions (De Haan 1976):

- Coulombic attraction as a result of opposite electric charges of adsorber and adsorbent
- other forms of physical bonding, due to London-van der Waals forces
- H-bonding, in which hydrogen atoms serve as a bridge between the adsorbent and a reactive group of organic matter
- metal-ion bonding, in which a metal ion serves as a bridge between adsorber and adsorbent, sharing bonds with both.

The reactions between the soil and the soil water system depend above all on the mineral composition of the soil, the specific surface of soil particles and the infiltration rate. The dark minerals formed at high temperatures, such as olivine, pyroxene or hornblende are more easily weathered than for example K-feldspar, quartz or muscovite, formed at lower temperatures.

The ease of weathering of minerals is directly dependent on their formation temperature and in general follows the order of crystallization of Bowen (1928).

One typical reaction in Finnish precambrian bedrock is the disintegration and transformation of calcium silicate, for example the feldspar mineral anortite:

$$Ca\,Al_2\,Si_2\,O_8 + 2H^+ + H_2O = Al_2\,Si_2\,O_5\,(OH)_4 + Ca^{2+} \qquad (20)$$

(Jacks 1978).

If strong acids such as sulfuric or nitric acid prevail in snow meltwater, the weathering reactions proceed as:

$$H_2SO_4 + \text{Ca-silicate} = Ca^{2+} + SO_4^{--} + CO_2 + H_2O + Al^{2+} \qquad (21)$$

(Elder 1981).

If calcite is present, it disintegrates in the following way:

In normal conditions,

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad (22)$$

Thus the concentration of bicarbonate increases.

In acid conditions the following reaction takes place:

$$CaCO_3 + H_2SO_4 = Ca^{2+} + SO_4 + CO_2 + H_2O \quad (23)$$

Since the weathering of the corresponding minerals are also due to the presence of carbon dioxide, the reactions will also proceed as follows:

$$Ca\,Al_2\,Si_2\,O_8 + 2CO_2 + 3H_2O = Al_2\,Si_2\,O_5\,(OH)_4 + Ca^{2+} + 2HCO_3^- \quad (24)$$

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \quad (25)$$

The latter reactions dominate in areas which are not exposed to acid precipitation (Soveri 1982 ed.).

In the following the changes occurring in meltwater during infiltration are examined for different materials separately and the differences in concentrations are estimated in sorted and unsorted soils. The infiltration water samples were taken using a lysimeter.

The *pH values* of the infiltration water were between 6.0 and 7.4 (median 6.8). The mean pH change after 170 cm vertical percolation with respect to the meltwater was +2.2 pH units. This considerable increase in the pH of the water was due mainly to the weathering and cation exchange of alkaline and earthalkaline metals from the soil minerals. The rapid change in the acidity of meltwaters occurs in the surface layer of the unsaturated zone above the groundwater surface, where weathering is also most rapid (Bjor and Teigen 1980). Soil weathering and nutrient balances are altered and processes such as solubilization and mobilization of minerals and metals are accelerated by increasing the acid concentrations in soil water.

The measured values of *electrical conductivity* were between 1.9 and 19.4 mS m^{-1} (mean 8.4 mS m^{-1} and median 6.5 mS m^{-1}), increasing from the corresponding mean value of the meltwater by about +6 mS m^{-1}. Increase in electrical conductivity indicates a corresponding increase in the amount of dissolved salts in the water during infiltration.

The concentrations of *calcium, magnesium, sodium* and *potassium* showed the greatest relative increases in the lysimeter water samples. The concentrations were about tenfold compared to the corresponding concentrations in the meltwater, and were mainly due to the weathering and ion exchange of silicate minerals. Calcium concentrations varied between 0.2 and 2.4 mg l^{-1} (mean 5.4 mg l^{-1} and median 3.1 mg l^{-1}), magnesium concentrations between 0.3 and 7.0 mg l^{-1} (mean 1.3 mg l^{-1} and median 0.8 mg l^{-1}), sodium between 0.5 and 3.7 mg l^{-1} (mean 1.6 mg l^{-1} and median 1.3 mg l^{-1}) and potassium between 0.1 and 2.6 mg l^{-1} (mean 1.1 mg l^{-1} and median 0.9 mg l^{-1}). The relationships between the mean concentrations of the different metals was:

$$Mg > 0.8\ K < 1.2\ Na < 4.2\ Ca \quad (19)$$

In comparison with the balance of materials in the meltwater, the concentration of calcium with relation to magnesium doubled, whereas that of potassium and sodium slightly decreased.

	SW	IW	IW − SW
$Ca_{\bar{x}}$ mg l^{-1}	0.4	5.4	+5.0
$Mg_{\bar{x}}$ mg l^{-1}	0.1	1.3	+1.2
$Na_{\bar{x}}$ mg l^{-1}	0.3	1.6	+1.3
$K_{\bar{x}}$ mg l^{-1}	0.2	1.1	+0.9

Calcium concentrations increased most in the infiltration water (+5 mg l^{-1}) and the concentrations of the other alkali and earthalkali metals also increased significantly. The leaching of calcium in soils increases drastically with increasing acidity of the precipitation (Bjor and Teigen 1980).

The occurrence and reactions of compounds of *nitrogen* and *phosphorus* in soil have been investigated in several different connections.

Nitrogen does not occur to any significant extent in the minerals of the bedrock and so it is not released in conjunction with weathering (Rönkä 1983). The naturally occurring nitrogen found in the soil is mainly formed as a degeneration product of organic material and as a result of deposition from the atmosphere (Soveri 1980).

Adsorption of nitrogen in the soil is slight. Only positively charged ammonium is adsorbed on soil particles. The negatively charged nitrate and nitrite ions can be transported with meltwaters to the groundwater. Particularly in fertilized soil they may cause pollution problems. Stewart (1970) and Pratt et al. (1972) assumed that nitrate moves in soil at the same rate as water.

The mean level of total nitrogen concentration in the infiltration water samples was about 30 % lower than that in the meltwater. The loss of nitrogen was due mainly to the upptake by vegetation. Nitrogen compounds also take part in biochemical processes. There is a continuous turnover of inorganic compounds into organic compounds and vice versa (Steenvoorden 1976).

The level of phosphorus is low also in the bedrock. The commonest phosphate mineral is

apatite, which is highly resistant to weathering (Pettijohn 1975).

Positively charged phosphorus compounds are retained rather efficiently by the surface soil layers. The transportation of these compounds to the groundwater is therefore only very slight. According to De Haan (1973), 90 % of total phosphate storage occurs in the upper 40 cm and 65 % in the upper 20 cm of the soil profile.

The concentration of total phosphorus decreased after infiltration to about 25 % of that in the meltwater. Like nitrogen, phosphorus is also an important plant nutrient, which is strongly adsorbed on soil particles.

	SW	IW	IW − SW
N_{tot} ($\bar{x}$) $\mu g\ l^{-1}$	736	585	−216
P_{tot} ($\bar{x}$) $\mu g\ l^{-1}$	18	5	− 13

Chloride concentrations were between 0.1 and 2.0 mg l^{-1} (mean 1.0 mg l^{-1} and median 1.0 mg l^{-1}). The occurrence of chloride in magma rock is at rather a low level (0.03 %) in Finland (Rankama and Sahama 1950). A certain amount of chloride is found in apatite, amphiboles and micas. Chloride reaches the soil mainly from marinogenic and anthropogenic sources via the atmosphere. The concentration of chloride in meltwater and infiltration water is of the same order.

Concentrations of *sulfate* are clearly lower in snow than in infiltration water, in which the concentrations vary between 0.6 and 65 mg l^{-1} (mean 11.2 mg l^{-1} and median 6.1 mg l^{-1}).

In the unsaturated zone in aerobic conditions the sulfide minerals are subject to weathering faster than silicate minerals (Smirnov 1954). During a dry spell, when the groundwater level is low, minerals may be oxidized in the unsaturated zone. For example, sulfate and hydrogen ions may be released from the oxidation of pyrite and then be carried to the groundwater by percolating water:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{++} + 4SO_4^{--} + 4H^+ \quad (26)$$

A lower groundwater level, resulting in an increase in the sulfate concentration and thus a decrease in pH, may be caused by climatic fluctuations or by human activities such as ditching, woodcutting or heavy graught on wells (Soveri 1982 ed., Jacks et al. 1984).

According to Englund (1983) the occurrence of sulfate in the groundwater reflects mainly the existence of pyrite in the bedrock. Sulfate ions can also be adsorbed by soils and redused by bacterial action. This reaction consumes acid and raises the pH of the soil water environment (Reuss 1976).

	SW	IW	IW − SW
Cl ($\bar{x}$) mg l^{-1}	0.8	1.0	+1.2
SO_4 ($\bar{x}$) mg l^{-1}	2.2	11	−8.8

Copper occurs in the bedrock mainly in association with sulfide ores ($CuFeS_2$). The differences in copper concentration between different rock types are great. In dark rock types copper is found in higher concentrations than in e.g. limestones and granites.

Copper readily forms stable compounds in poorly soluble acidic conditions (pH 3.5—5.0). Furthermore it may also form bonds with other heavy metals with the aid of humus molecules (Stevenson 1975). Of the salts of copper, sulfates, chlorides and nitrates are easily soluble whereas carbonates, hydroxides, oxides and sulfides are poorly soluble.

The copper concentrations in the lysimeter water samples varied between < 1 and 70 $\mu g\ l^{-1}$ (mean 14 $\mu g\ l^{-1}$ and median 6 $\mu g\ l^{-1}$). The change with relation to the median value of copper concentration in the meltwater samples was small (+ 2 $\mu g\ l^{-1}$).

Lead is the most abundant of the heavy metals with an atomic number greater than 60. Galena (PbS), is the most abundant form of lead in the natural state. Lead is also found as cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Of the various lead compounds, sulfate is particularly weakly soluble in water. Dissolution of lead from the bedrock is also rather slight.

According to Kauranne et al. (1961) lead anomalies in humus seems to be caused mostly by transport of glacial ice. The vertical diffusion of heavy metals in till is small, therefore these concentrations seldom are high directly above the ore exposure.

According to various reports (e.g. Salmi 1969, Tanskanen 1977 and Sillanpää 1982), airborne lead is retained very efficiently by the organic surface layer of the soil. Due to this strong adsorption at the surface, the leaching of lead to lower soil levels is rather slight.

The lead concentrations of the lysimeter water samples varied between < 1 and 28 $\mu g\ l^{-1}$ (mean 5 $\mu g\ l^{-1}$ and median 3 $\mu g\ l^{-1}$). The median concentration of lead in the infiltration water samples was 3 $\mu g\ l^{-1}$ lower than in the meltwater, indicating adsorption of atmospheric lead into the soil.

Manganese occurs in mineral form usually as insoluble manganese dioxide (MnO_2), but reacts for example with sulfur dioxide in the following way:

$$2\,MnO_2 + 3\,SO_2 \rightarrow MnSO_4 + MnS_2O_6 \qquad (27)$$

with the proportion of soluble manganese sulfate. In nature manganese often occurs with iron containing minerals (Tiitinen 1981).

The manganese concentrations of lysimeter water samples varied between < 1 and 810 $\mu g\ l^{-1}$ (mean 132 $\mu g\ l^{-1}$). The level of manganese concentration in infiltration water was clearly higher than in meltwater.

Aluminium is commonly found in the bedrock and soil, for example in feldspars, micas and hornblende. Due to the pH range of 3—6 in such environments, the aluminium released is found either as hydroxides or in clay minerals of the kaolinite, montmorillonite or illite type. When the sulfate concentrations of infiltration water reach a sufficiently high level the hydroxides or silicates of aluminium are transformed into basic sulfates, mainly to Al OH SO_4. The reaction, as proposed by Eriksson (1981) is the following:

$$Al(OH)_3 + 2\,H^+ + SO_4^{--} \rightarrow Al\,OHSO_4 + 2H_3^= \qquad (28)$$

With the exception of sulfate, the compounds formed by aluminium in presence of strong acids are all soluble. The double salts formed in conjunction with the alkaline metals are also soluble. Aqueous solutions of aluminium ions are weak acids. One of the effects of soil acidification is the mobilization of aluminium. The solubility of this metal is pH dependent, with a minimum solubility at about pH 6 (May et al. 1979).

The aluminium concentrations of the lysimeter water samples were between 10 and 300 $\mu g\ l^{-1}$ (mean 87 $\mu g\ l^{-1}$ and median 50 $\mu g\ l^{-1}$). In comparison with the meltwater samples of 1982 and 1983 the aluminium concentrations in the lysimeter water samples were clearly higher than in the snow.

The median concentrations of copper and lead did not change significantly during infiltration, from which it can be concluded that at least part of the lead and copper in the infiltration water originates from the atmosphere. On the other hand, aluminium and manganese were increased when water filtered through the soil in comparatively large amounts. The concentrations in the water taken from lysimeter were clearly higher than those in the snow. The weathering of minerals, as well as their solubility in water, obviously affected the concentrations ot these metals (Table 15).

The following interrelationship was obtained between the metal concentrations of the infiltration water samples:

Table 15. Comparison of the median concentrations of copper, manganese, lead and aluminium in snow (SW) and in infiltration water (IW).

Parameter	Concentration $\mu g\ l^{-1}$		IW—SW
	SW	IW	
Cu	4	6	2
Mn	20	39	19
Pb	6	3	−3
Al	26	50	24

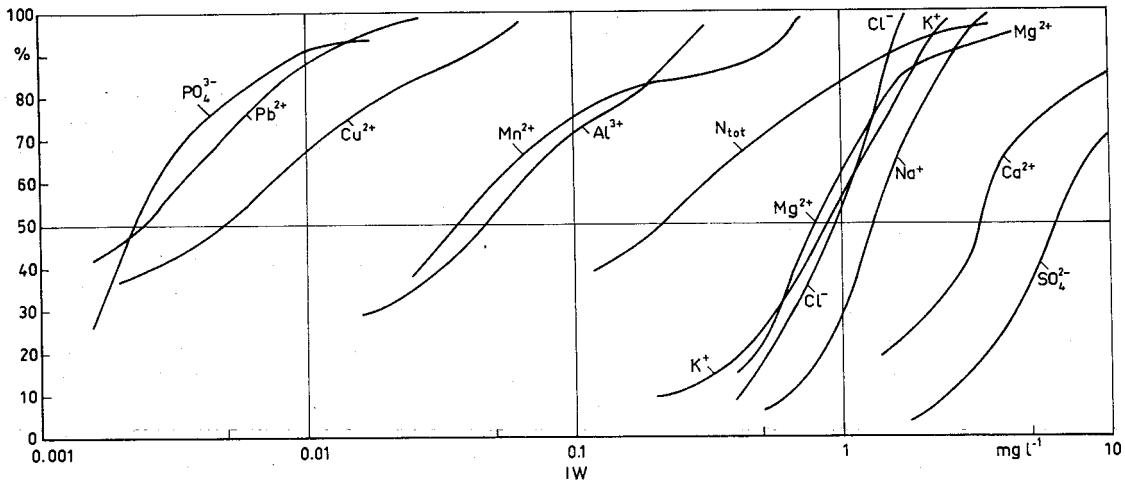

Fig. 16. Cumulative distribution of concentration for various constituents of infiltration water at groundwater stations during the years 1976—1981.

$$Pb < 2Cu < 13\,Mn < 16.7\,Al \quad (29)$$

Cumulative distribution of concentration for various constituents of infiltration water at groundwater stations during the years 1976—1981 are given in Fig. 16.

The relationships between the mean concentrations of cations and anions of whole data were:

$$SO_4 > Ca > Na > Cl \approx Mg > K > N_{tot} > Al > Mn > Cu > Pb > PO_4 \quad (30)$$

4.21 Concentration patterns in different soil types

The usual statistical parameters of the pH, electrical conductivity and elemental concentrations of infiltration water are presented in Table 16.

The interrelations between the different lysimeter water analysis results were examined with the aid of a correlation matrix (Table 17). The correlation coefficients describe the interrelationship between the concentrations of the data pairs in the meltwater (r_1) and in the infiltration water (r_2). The following regression functions were calculated for the data pairs of the infiltration water with the best correlations:

		r_2	(r_1)	
$SO_4 = 1.7 \cdot Ca + 1.7$		0.73***	(0.43***)	(31)
$Cl = 0.2 \cdot Na + 0.6$		0.48***	(0.53***)	(32)
$K = 0.1 \cdot Ca + 0.7$		0.68***	(0.34***)	(33)
$Mg = 0.3 \cdot K + 0.7$		0.59***	(0.52***)	(34)
$\gamma_{25} = 2.0 \cdot Mg + 6.0$		0.54***	(0.10)	(35)
$\gamma_{25} = 0.2 \cdot SO_4 + 6.2$		0.66***	(0.70***)	(36)
$\gamma_{25} = 4.2 \cdot K + 3.9$		0.61***	(0.17**)	(37)
$\gamma_{25} = 0.7 \cdot Ca + 5.2$		0.74***	(0.23***)	(38)

Table 16. Infiltration water analysis results at the lysimeter field stations during the period 1978—1982 (see list of symbols).

Parameter	Unit	n	min	max	mean	median	S	$S_{\bar{x}}$	$S/\bar{x}$
pH		65	6.0	7.4	6.8	6.8	0.3	0.04	0.05
γ_{25}	mS m^{-1}	64	1.9	19.4	8.4	6.8	4.6	0.57	0.55
SO_4	mg l^{-1}	57	0.6	65.0	11.2	5.7	13.3	1.77	1.19
Cl	mg l^{-1}	64	0.1	2.0	1.0	0.9	0.4	0.05	0.44
Na	mg l^{-1}	53	0.5	3.7	1.6	1.3	0.8	0.11	0.51
K	mg l^{-1}	53	0.1	2.6	1.1	1.0	0.7	0.09	0.63
Ca	mg l^{-1}	53	0.2	24.0	5.4	3.1	5.9	0.81	1.09
Mg	mg l^{-1}	54	0.3	7.0	1.3	0.8	1.4	0.18	1.05
N_{tot}	μg l^{-1}	64	1	4226	585	200	927	116	1.58
P_{tot}	μg l^{-1}	58	1	30	4.7	2.0	6.4	0.85	1.36
Cu	μg l^{-1}	49	<1	70	13.6	5.5	18.5	2.6	1.36
Mn	μg l^{-1}	56	<1	810	131	39	206	27.5	1.57
Pb	μg l^{-1}	52	<1	38	4.9	3.0	6.1	0.84	1.25
Al	μg l^{-1}	38	10	300	87	50	97	18.3	1.11

Table 17. Correlation matrix of infiltration water samples.

	pH	γ_{25}	P_{tot}	SO_4	Cl	Na	K	Ca	Mg	N_{tot}	Al	Cu	Mn	Pb
pH	1.00													
γ_{25}	0.25	1.00												
P_{tot}	0.14	0.02	1.00											
SO_4	0.36**	0.66***	0.16	1.00										
Cl	0.03	0.28*	0.07	0.01	1.00									
Na	0.02	0.30*	0.46**	0.01	0.48***	1.00								
K	0.17	0.61***	0.23	0.45**	0.25	0.26	1.00							
Ca	0.11	0.74***	0.11	0.73***	0.32*	0.15	0.68***	1.00						
Mg	0.22	0.54***	0.01	0.15	0.34*	0.40**	0.59***	0.51***	1.00					
N_{tot}	0.12	0.09	0.01	0.08	0.08	0.41**	0.14	0.02	0.26	1.00				
Al	0.34	0.04	0.11	0.04	0.28	0.08	0.22	0.06	0.02	0.03	1.00			
Cu	0.19	0.24	0.14	0.00	0.36*	0.04	0.17	0.25	0.16	0.07	0.03	1.00		
Mn	0.19	0.27*	0.07	0.04	0.10	0.33*	0.32*	0.18	0.50***	0.31*	0.23	0.20	1.00	
Pb	0.15	0.05	0.32*	0.13	0.21	0.09	0.04	0.20	0.19	0.03	0.06	0.17	0.07	1.00

By comparing the significance levels of the correlation coefficients between the quality parameters in the meltwater and in the infiltration water, a rough estimate is obtained of the anthropogenic or geological cause-effect relationships of the different material balances.

According to the compared correlations, the soil has a clear effect on the relative ionic concentrations of sulfate and calcium in infiltration water. Increased deposition of sulfate increases the weathering of calcium and thus also its leaching from the soil. The alkali and earthalkali metals liberated from the mineral material in conjunction with weathering significantly affect the total ionic concentration of the infiltration water, which is revealed in a clear correlation with electrical conductivity. A corresponding dependence was not observed in the meltwater.

The airborne inputs were clearly observable in the infiltration water in the case of chloride and sodium. The significance levels of correlations between the concentrations of these mobile and unreactive ions did not undergo significant change during infiltration ($r_1 = 0.53^{***}$ and $r_2 = 0.48^{***}$). The effect of atmospheric sulfate on the electrical conductivity of meltwater was statistically most significant ($r_1 = 0.70^{***}$).

No interdependence between heavy metal concentrations of the infiltration water samples were recorded for any pair of data. On the other hand a highly significant correlation was obtained between many of the metals in the examination of the data for meltwater. In a regional investigation by Water District of National Board of Waters the correlations between the metals were in many cases further clarified. This indicates the importance of regional factors, particularly in the deposition of metals and therefore also in their relative concentrations in the meltwater. However, the original ionic proportions between the different metals change considerably in the soil during infiltration. These changes are considered in more detail in Section 4.31.

The change in the substance concentrations of meltwater during infiltration was examined by a test series in sandy soil at the Siuntio lysimeter field in the spring of 1983. At the same time the movement of the infiltrating pulse of the meltwater in the soil was monitored by the neutron measurement method.

On the basis of soil moisture observations, the percolation of meltwater had advanced to a depth of 40 cm by March 15 and to 160 cm by March 31. On April 3 the water began to filter through into the lysimeter vessel. Samplings were carried out on the seventh, fourteenth and twenty-sixth of April.

Soil moisture measurements were made in both the lysimeter vessel and the undisturbed reference point outside the vessel in conjunction with the sampling. The progress of infiltration was almost identical in the disturbed and undisturbed soil (Fig. 17).

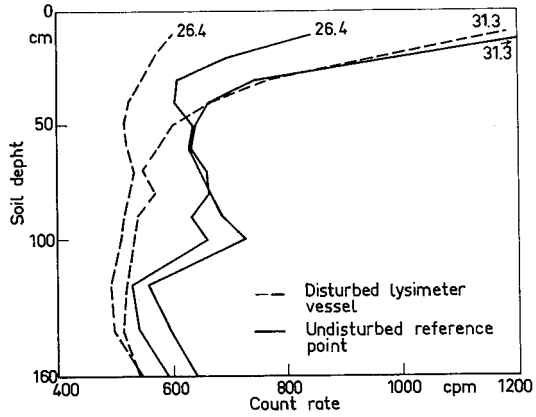

Fig. 17. Soil moisture in a lysimeter vessel and at an undisturbed reference point at different stages of infiltration at the Siuntio lysimeter field in 1983.

The substance contents of the filtered water varied between different sampling times. At the early stages of infiltration the concentrations of metals and sulfate and of alkali and earthalkali metals were higher than towards the end of melting period.

During the spring, summer and autumn of 1984 a lysimeter test series was carried out in Siuntio, Perniö and Kolmisoppi. The soil type in the lysimeter was coarse sand at Siuntio, stony gravel at Perniö and sandy moraine at Kolmisoppi. The analysis results of infiltration water are presented in Tables 18, 19 and 20, in which I_r also indicates the rate of infiltration in mm d^{-1}. The infiltration rates were estimated from the recorder curves.

One of the reasons for the strong mobilization of substance during the spring infiltration is, however, the weathering taking place in the soil during winter, when infiltration and leaching do not occur. The first meltwater efficiently leaches many of the products of weathering (e.g. Ca, Mg, SO_4 and Al) deeper into the soil and thence to the groundwater.

Dissolution of materials from soil minerals in the soil water is slight during the snowmelt period. The infiltration test series also indicated that material concentrations in infiltration waters usually decreased with decreasing infiltration rate and correspondingly increasing solubility time. When infiltration rates were high, the infiltrated water

Table 18. Concentrations in material balances during infiltration at the Siuntio (1) groundwater station in 1983 and 1984.

Sampling date		Infiltration rate and quality parameters																			
		I_r mm d^{-1}	pH	γ_{25} mS m^{-1}	Alk. mmol l^{-1}	Na mg l^{-1}	K mg l^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	Cl mg l^{-1}	SO_4 mg l^{-1}	NO_3-N $\mu g\ l^{-1}$	PO_4-P $\mu g\ l^{-1}$	F $\mu g\ l^{-1}$	Al $\mu g\ l^{-1}$	Fe_{tot} $\mu g\ l^{-1}$	Cu $\mu g\ l^{-1}$	N_i $\mu g\ l^{-1}$	Pb $\mu g\ l^{-1}$	Mn $\mu g\ l^{-1}$	SiO_2 $\mu g\ l^{-1}$
1983	8.4.	3.0	6.9	9.8	0.81	1.1	4.7	3.7	0.7	—	—	34	—	580	84	47	38	1	2	5	6.6
	14.4.	0.8	7.0	6.5	—	0.8	3.9	2.7	0.5	5.1	5.7	40	—	—	330	—	< 1	—	<1	20	—
	26.4.	1.0	6.9	8.3	—	0.8	4.1	3.1	0.5	1.5	5.7	270	—	—	26		3		1	4	—
1984	22.3.	11.0	—	—	—	7.3	3.3	19.0	11.0	—	—	—	—	240	—	—	11	—	<1	—	34.5
	18.4.	7.0	7.1	—	—	1.3	6.7	10.1	2.1	2.2	5.0	74	—	40	60	—	—	—	—	10	8.1
	27.4.	2.0	6.9	7.0	0.50	0.8	3.4	2.3	0.1	—	—	63	—	50	28	—	—	—	2	6	5.1
	14.5.	1.6	6.9	6.2	0.46	0.7	3.4	2.8	0.6	—	5.2	70	< 5	20	60	27	—	1	1	9	5.6
	4.6.	0.6	6.7	9.6	0.78	0.9	4.3	3.4	0.6	—	—	91	14	50	45	18	< 1	2	<1	2	6.2
	26.6.	0.3	7.0	6.2	0.48	0.8	3.9	2.6	0.5	—	—	110	5	60	57	50	—	<1	<1	12	5.1
	7.8.	0.5	—	—	—	—	—	—	—	—	—	—	—	70	4	—	—	—	<1	—	7.6
	20.8.	0.3	7.4	11	1.0	0.8	3.4	3.1	0.7	1.1	5.2	180	5	50	28	15	—		<1	17	5.1
	24.8.	0.1	—	—	—	1.5	5.6	4.0	0.7	—	—	—	—	40	20		—	4	<1	5	5.7
	21.9.	1.5	—	—	—	—	—	—	—	—	—	—	—	—	42		—		<1	—	7.9
	8.10.	1.0	7.0	7.8	0.66	1.2	4.6	2.8	0.5	—	5.6	190	4	50	110	25	—	5	1	< 5	7.4
	24.10.	1.5	7.0	11.0	0.28	0.8	3.8	1.9	0.4	—	6.4	93	< 5	—	200	110	—	3	<1	23	—
	7.11.	2.0	6.9	4.4	0.19	—	—	—	—	—	6.3	44	2	—	—	71	—	—	—	< 5	—
	27.11.	0.8	7.1	4.5	0.24	0.8	3.4	1.7	0.2	—		59	< 5	—	—	—	—	—	—	—	—

Table 19. Concentrations in material balances during infiltration at the Perniö (6) groundwater station in 1984.

Sampling date		Infiltration rate and quality parameters																			
		I_r mm d^{-1}	pH	γ_{25} mS m^{-1}	Alk. mmol l^{-1}	Na mg l^{-1}	K mg l^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	Cl mg l^{-1}	SO_4 mg l^{-1}	NO_3-N $\mu g\ l^{-1}$	PO_4-P $\mu g\ l^{-1}$	F $\mu g\ l^{-1}$	Al $\mu g\ l^{-1}$	Fe_{tot} $\mu g\ l^{-1}$	N_i $\mu g\ l^{-1}$	Pb $\mu g\ l^{-1}$	Mn $\mu g\ l^{-1}$	Se $\mu g\ l^{-1}$	SiO_2 $\mu g\ l^{-1}$
1984	17.4.	7.5	6.8	17.2	1.53	1.3	0.6	2.9	1.0	1.8	13.1	100	4	40	38	—	1	12	27	<0.5	6.5
	14.5.	1.3	—	—	—	1.2	0.5	1.8	0.7	—	—	—	—	60	12	—	<1	<1	—	—	6.6
	31.5.	1.3	6.6	8.8	0.58	1.3	0.5	2.0	0.8	—	—	94	—	60	22	—	2	<1	22	—	6.6
	26.6.	0.2	7.2	7.6	0.42	1.4	0.5	2.1	0.8	—	12	41	—	80	54	15	<1	<1	11	—	5.2
	27.7.	4.0	7.2	11.0	0.12	1.6	0.6	2.5	0.8	—	11	57	—	70	4	—	<1	<1	25	—	7.6
	17.9.	1.3	7.3	9.4	0.64	1.5	0.6	2.2	0.8	2.1	11	43	<5	—	42	< 5	2	1	7	—	7.9

Table 20. Concentrations in material balances during infiltration at the Kolmisoppi (45) groundwater station in 1984.

Sampling date		Infiltration rate and quality parameters																				
		I_r mm d^{-1}	pH	γ_{25} mS m^{-1}	Alk. mmol l^{-1}	Na mg l^{-1}	K mg l^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	Cl mg l^{-1}	SO_4 mg l^{-1}	NO_3-N $\mu g\ l^{-1}$	PO_4-P $\mu g\ l^{-1}$	F $\mu g\ l^{-1}$	Al $\mu g\ l^{-1}$	Fe_{tot} $\mu g\ l^{-1}$	Cu $\mu g\ l^{-1}$	N_i $\mu g\ l^{-1}$	Pb $\mu g\ l^{-1}$	Mn $\mu g\ l^{-1}$	Se $\mu g\ l^{-1}$	SiO_2 $\mu g\ l^{-1}$
1984	24.4.	12	6.6	10.1	0.45	0.8	1.8	7.9	2.5	0.6	21.2	83	300	40	460	4900	4	5	<1	160	<0.5	11.7
	2.5.	6	6.9	8.0	0.62	0.4	1.3	3.9	0.9	0.5	5.0	69	1	40	53	110	2	3	4	93	<0.5	10.3
	7.5.	5.5	6.6	7.8	0.46	0.5	1.2	3.8	0.9	0.5	5.1	72	0	30	53	1	1	7	<1	1	<0.5	10.1
	15.5.	1.0	6.8	8.9	0.71	0.4	1.4	4.3	1.0	0.6	5.4	57	1	30	18	16	<1	7	1	86	<0.5	10.5
	11.6.	0.5	6.7	12.1	1.08	0.6	1.8	5.3	1.3	—	6.5	4	—	50	11	79	1	14	1	230	—	9.5
	29.10.	2.3	6.3	11.4	0.94	1.5	1.1	1.8	1.0	0.3	6.1	31	1	—	20	3	1	< 1	<1	35	—	—

also had a higher material concentration. This generalization also applied to autumn infiltration, during which material concentrations increased after the weathering taking place during the summer season.

When the amount of infiltration is very small the concentrations of different elements often increase due to the correspondingly long period of contact between the mineral soil and the soil water. In this case the soil water material balance is affected mainly by solubility processes, whereas during the spring thaw the weathering products liberated during the winter season are washed out. The relationship between the calcium concentration of soil water and the rate of infiltration is presented in Fig. 18 during spring, summer and autumn infiltration.

The material budget of the infiltration water samples were examined in sorted and unsorted soils. Sorted soils are composed of only one or only a few adjoining particle size fractions include in this paper e.g. highly porous sand and gravel soil types, whereas unsorted soils have a wide array of particle fractions and the exemplified by more impervious till soil types. The mean concentrations are presented in Table 21.

Clear differences between the material concentration of the filtered water were observed in sorted and unsorted soils. Concentrations of sulfate, copper and lead were greater in coarse and sorted soils than in unsorted soil types. These materials are all mainly of atmospheric origin. In coarse-grained soils the rate of infiltration is much greater than in fine soils, so that the dissolution of these ions from the mineral soil to the water, as well as their adsorption on mineral grain surfaces, is less pronounced. The concentrations of the typical products of weathering, namely calcium, potassium, magnesium, sodium and aluminium, were clearly greater in unsorted than in sorted soils.

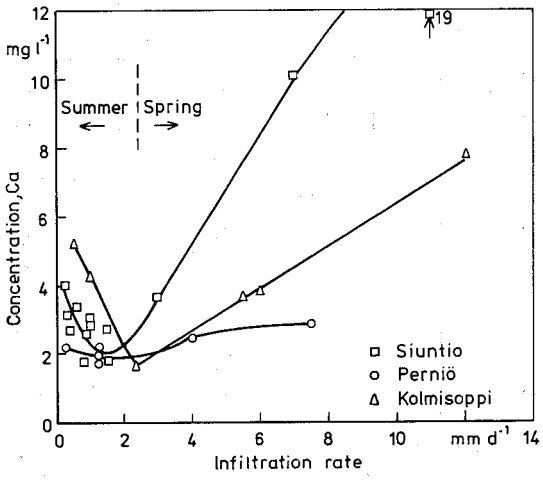

Fig. 18. Dependence of calcium concentration of infiltration water on infiltration rate at Kolmisoppi, Perniö and Siuntio station in 1984.

4.3 Unsaturated zone and acidity processes

The unsaturated soil zone affects the formation and the quality of groundwater. The substance concentration in the meltwater changes considerably as the water filters through the unsaturated zone. Hydrogen atoms of the acidic meltwater tend to be replaced by base cations from the soil, with the result that the alkaline content of the soil water increases.

According to results of the lysimeter experiments the median pH-value of the infiltration water increased on average by 2.2. pH units in comparison with the meltwater. Increase in pH also reflects the ability of the soil to neutralize acids. The phenomenon is in dynamic equilibrium as long as the buffering processes of the soil are sufficient to react with the hydrogen ions of the incoming water. With increase in the acidity of the water the extraction of materials from the mineral

Table 21. Mean concentrations in infiltration water samples in sorted and unsorted soil types.

Soil type	Chemical parameters													
	pH	γ_{25} mS m^{-1}	P_{tot} µg l^{-1}	SO_4 mg l^{-1}	Cl mg l^{-1}	Na mg l^{-1}	K mg l^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	N_{tot} µg l^{-1}	Al µg l^{-1}	Cu µg l^{-1}	Mn µg l^{-1}	Pb µg l^{-1}
Sand, gravel	6.9	8.2	4.9	15.2	0.9	1.5	0.9	5.2	1.0	298	100	25	95	6
(n)	(41)	(41)	(38)	(36)	(41)	(32)	(32)	(32)	(33)	(38)	(20)	(33)	(36)	(33)
Till, silt	6.6	10.9	3.5	6.5	1.2	1.8	1.5	8.8	2.1	1030	250	14	246	5
(n)	(16)	(16)	(13)	(14)	(16)	(15)	(15)	(15)	(15)	(16)	(6)	(13)	(13)	(13)
$\bar{x}$	6.8	10.1		11.6	1.1	1.9	1.5	6.9	1.4	520	132	22	129	6

soil also increases, upon which the alkalinity and pH value again become greater. Only when the buffering capacity of the soil is exceeded does the pH of the soil water solution itself begin to decrease.

In Finland the natural buffering capacity of the mineral soil is rather low. The precambrian bedrock is poor in calcium and consists mainly of acidic rocks. Furthermore the soil is rather thin and its unsaturated zone is shallow, so that the contact time of infiltration water with the mineral soil is short. For these reasons the groundwater in Finland is particularly susceptible to acidification. Some variation in the ability of the soil to neutralize acidic meltwaters does of course occur between different areas of the country, depending on the depth of the unsaturated zone and on the relative proportions of acidic and alkaline minerals in the soil.

4.31 Chemical input and output in the unsaturated zone

The surface of the soil functions as a kind of chemical filter between the meltwater and the groundwater. In this layer a number of different chemical reactions takes place (e.g. ion exchange, adsorption and precipitation). The final chemical balance of the soil water is dependent on the overall effect of these reactions.

An input-output investigation (Input = Output ± Change in unsaturated zone) was carried out of the change in concentration of certain materials in meltwater during infiltration at several lysimeter stations. The results have been collected into Table 22. The change in concentration in the infiltration water in relation to the corresponding concentration in the meltwater is presented in sorted and unsorted soil types.

Acid meltwater continuously causes changes in the substance balance of soil water. As a result of weathering processes and of cation exchange between the minerals and soil solution, calcium, magnesium and aluminium ions are released to the soil water and hydrogen, ammonium and nitrate ions are precipitated on to soil particles and absorbed by minerals (Seip 1980). Cation exchange is a rapid process compared to weathering.

The material concentrations of infiltration water increase in almost all cases in comparison with the corresponding concentrations in meltwater. The greatest changes were observed in alkali and earthalkali metals and in the pH of the water. Significant increase in pH in the infiltration water can partly be explained by the fact that the hydrogen ions of the acid meltwaters are replaced efficiently by base cations from the soil particles.

Of the anions, the leaching of sulfide was the

Table 22. The input-output concentration balance of meltwater and infiltration water at different lysimeter fields.

Lysimeter field	Year	IW—SW									
		pH	γ_{25} mS m^{-1}	SO_4 mg l^{-1}	Cl mg l^{-1}	Na mg l^{-1}	K mg l^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	Cu µg l^{-1}	Mn µg l^{-1}
Oripää	1982	2.0	0.7	+4.0	0.1	0.7	0.1	3.0	0.8		31
Jämijärvi	1978	2.6	4.5	3.8	0.2	0.6	0.5	1.7	0.6	—	−17
Valkeala	1982	2.4	10.0	0.9	0.1	0.6	—	1.6	—	1	—
Parikkala	1982	2.0	3.6	0.6	0.2	—	—	—	—	—	—
Pistohiekka	1981	2.0	5.7	8.2	0.8	1.5	1.2	2.3	1.2	−3	—
Naakkima	1981	1.6	2.5	3.8	0	0.6	1.0	2.1	0.5	1	−15
Kangaslahti	1980	2.6	0.7	2.1	0.4	0.5	0.1	0.3	0.3	49	28
Kuuksenvaara	1978	2.7	8.8	17.5	0.1	0.6	1.1	7.3	0.7	12	38
Jaamankangas	1978	2.4	8.5	18.3	0.4	1.3	0.9	10.2	1.7	1	−14
Juutilankangas	1980	2.8	10.0	25.2	0.1	1.2	0.9	10.0	1.1	15	6
Pyhäntä	1982	1.9	4.1	0.9	0	2.7	1.7	1.4	0.4	48	11
Ruukki	1980	1.7	2.2	3.0	0.2	0.4	0	0.2	0.5	0	—
Alakangas	1982	2.0	1.6	3.6	−0.2	0.2	0.7	1.9	1.5	−2	—
Nellim	1981	1.4	9.5	—	1.2	2.7	0.4	3.3	1.0	5	−14
Sorted soils	$\bar{x}$	2.3	4.1	6.2	0.2	1.0	0.7	3.5	0.8	12	6
Kuuminainen	1982	2.3	4.0	6.1	0.3	0.6	0.7	3.5	0.8	19	−33
Heinävesi	1981	1.5	3.9	4.2	0.3	1.8	1.6	2.2	0.8	1	6
Akonjoki	1980	2.5	2.8	1.1	0.9	2.1	1.9	3.6	1.3	29	46
Vehkoo	1981	2.2	4.5	1.3	0.4	1.6	0.5	1.9	0.4	5	24
Kolmisoppi	1979	2.1	7.0	13.5	0.9	1.4	1.7	13.7	1.5	9.0	68
Lumiaho	1982	1.8	10.1	6.4	1.0	2.4	0.8	3.9	1.2	−1	—
Unsorted soils	$\bar{x}$	1.7	2.8	2.5	0.4	1.6	1.2	5.4	1.0	10	12

greatest. This ion occurs in the form of sulfate mainly as a result of the weathering of sulfide minerals and derived from litter and organic layer (Barry et al. 1984). Changes in chloride concentrations were slight throughout the data of this investigation. The release of this ion from the soil and its adsorption on soil particles are both insignificant.

Concentrations of infiltration water were in almost all cases lower than in the corresponding meltwater. According to the lead balance, the content of this metal in the infiltration water originates mainly from the atmosphere. Lead is known to be witheld by the surface soil layer, while its movement in the mineral soil is only slight (Kauranne et al. 1977; Tanskanen 1977; Sillanpää 1982).

The balance of copper and manganese was also in some cases negative (the concentration was greater in snow than in infiltration water), but in most cases the concentrations of these metals clearly increased during infiltration. The contents of copper and manganese in infiltration water are due partly to deposition from the atmosphere and partly to dissolution from the mineral soil layer.

5. SUBSTANCE CONCENTRATIONS IN GROUNDWATER AND THEIR TEMPORAL AND SPATIAL VARIATIONS

The quality of groundwater is determined largely by the hydrogeological and hydrometeorological conditions of groundwater recharge area. The elemental composition of the groundwater often reflects the mineralogy of the soil and bedrock of the recharge area, as well as airborne loading. The effect of bedrock and soil on groundwater quality has been investigated in Finland in several studies (e.g. Lahermo 1970, Hyyppä 1973, Soveri and Soveri 1981, and Rönkä 1983). However, the effect of atmospheric impurities has been studied much less (Soveri 1980).

Overall groundwater quality in a groundwater system at a given point in space and time is composed of the sum of several partial factors. Each partial quality has its own specific evolution within three interconnected subsystems, namely transport, matter and conversion processes (Engelen 1981):

1. Transport
   - — permanent or transient flow under laminar or turbulent conditions.
2. Matter
   - — soil and rock types, each with its own spatial pattern
   - — chemical composition and isotropic or non-isotropic characteristics.
3. Conversion
   - — physical, chemical and biological processes changing the quality.

In most natural groundwater systems, it is the chemical and biological processes which act from point to point within the system and ultimately determine the chemical composition of the soil water and groundwater. When these processes are relatively homogeneous and spatially continuous, it is possible to define a systematic cyclic annual variation in the major ion concentrations within a groundwater system for different soil types.

The chemical processes include dissolution of the porous medium, precipitation of mineral phases, ion exchange between the pore fluid and the porous medium and osmosis or reverse osmosis. Biological processes, which can control water chemistry by the addition or removal of CO_2 and by bacterial reduction of the sulfate ion, may also be of considerable importance.

The rate of accumulation and the relative abundance of dissolved constituents in groundwater depends to a large extent on the dissolution kinetics of the porous medium. Mineral dissolution rates are a complex function of several variables, such as pH, temperature, mineral structure and the equilibrium state of the fluid with respect to that mineral. From a kinetic viewpoint, dissolution proceeds until chemical equilibrium is achieved between the mineral phase and the pore fluid (Schwartz 1974).

The mobility of an element in the hydrosphere is in general determined by the solubility of its various compounds, the tendency of its ions to deposit on rocks adsorption and ion exchange, and the degree to which it is bound in the biosphere. Geochemical bonding is determined by the ionic potential of the element, i.e. the ratio between ionic charge and ionic radius (Wickman 1944).

As a measure of the mobility of an element in water the mobility coefficient K_x proposed by Perel'Man (1961) can be simplified used. K_x is the ratio between the concentration of an element X in water and the concentration in the rock through which the solution is flowing. If the concentration of the element X in the water (M_x) is given in grams per litre and the content nx in the rock in wt %, then $K_x = (M_x \cdot 100)/a \cdot nx$, in which a is the

sum of the dissolved mineral substance in water in grams. Large values of K_x indicate intensive release from the rock and mobility of the element in solution (Matthes 1982).

The method of Perel'Man gives an approximate picture of the mobilization of different materials and is best suited to sorted sand and gravel soil types.

The amounts of different mineral compounds in moraine and bedrock are many times greater than those appearing in sorted soil types. The use of K_x in the quantitative determination of the mobilization of different materials therefore becomes more difficult.

The commonest elements in igneous rocks, such as silicon, aluminium and iron as well as lead, have low mobility in the hydrosphere. Chlorine and sulfate are very mobile and widespread in the hydrosphere. Calcium is mobile to some extent and sodium is considerably more mobile than potassium, although both occur in almost equal amounts in the primary igneous material.

Nearly all groundwaters in Finland, both shallow and deep, originate from rain and melted snow infiltrating through the soil. The quality of groundwater at a given point in an aquifer thus depends on the intergrated effects of a number of factors, such as (Englund 1983):

1. the chemistry of the input water
2. the pathway of water through the aquifer
3. subsurface soil and rock types encountered during infiltration
4. variations in residence time or flow velocity along the infiltration pathway
5. hydrodynamic dispersion
6. rates and threshold values of physical, chemical and biological processes

This study is concerned mainly with the effects of the factors 1—4 above.

5.1 Chemical composition of groundwater

In the following, elemental concentrations in groundwater are investigated individually and their changes are compared with corresponding changes in the infiltration water.

The *pH values* of groundwater varied between 4.5 and 8.8 (median 6.3). The lowest pH values of groundwater were observed in the sulfide regions of Ostrobothnia (Kälviä and Laihia). Lower pH values were also observed in the granite regions of southern Finland than elsewhere. In the alkaline bedrock regions of northern Finland the mean values of groundwater pH were higher than in other parts of the country.

The mean change with respect to the pH of the infiltration water was −0.5 units. The areas investigated were shallow aquifers, in which the circulation time of the water was short. The pH value is usually lower in shallow wells than in deep circulating groundwaters (Englund 1983, Jacks et al. 1984).

In bedrock groundwater, in which the circulation time of the water is long, pH values are usually higher, as in the soil groundwater discussed above. According to Rönkä (1983) the mean pH values of bedrock groundwater vary according to the type of rock between 5.3 and 9.0 (mean 6.8).

The *alkalinity* values of groundwater varied between 0.01 and 4.84 mmol l^{-1} (mean 0.31 mmol l^{-1} and median 0.22 mmol l^{-1}). The alkalinity, i.e. buffer capacity, of Finnish groundwater is usually rather low. Of the alkalinity concentrations observed in the data of this study, 99 % were below 1.6 mmol l^{-1}.

Alkalinity is the capacity factor, which represent, respectively, the acid-neutralizing capacity of an aqueous system (Stumm and Morgan 1981), which is usually determined by acidimetric titration to a pH value of 5.4. (Bergström et al. 1985)

The alkalinity of Finnish groundwater is determined by the concentrations of bicarbonate and carbonate. In certain conditions (pH > 8.3), hydroxyls have a significant effect. The alkalinity system of soil water and groundwater buffer the water against the effects of hydrogen ions.

The sensitivity of groundwater to acidification is dependent on the alkalinity of the water. Alkalinity is a measure of the degree to which water resists changes in pH on the addition of strong acid, and loss of alkalinity can therefore be used as a tool for studying the extent of influence of the processes of acidification. E.g. Henriksen (1979) has defined acidification as loss in alkalinity. It is operationally defined as the difference between "preacidification" alkalinity and present alkalinity.

$$\text{Acidification (Ac)} = \text{Alk}_o - \text{Alk}_t, \qquad (39)$$

where

Alk_o = original alkalinity (estimated from the sum of the concentrations of non-marine calcium and magnesium in the water)

Alk_t = present alkalinity

Values of *electrical conductivity* were between 0.2 and 53.0 mS m^{-1} (mean 6.0 mS m^{-1} and median 4.1 mS m^{-1}). Conductivities in groundwater were about 2 mS m^{-1} lower than in the infiltration

water. As the water infiltrates through soil, its salts are partly enriched, or salts may be recrystallized in the unsaturated zone above the groundwater.

In bedrock water electrical conductivity is usually higher than in soil groundwater. According to Rönkä (1983) the mean conductivity of bedrock groundwaters is 28.0 mS m^{-1}, varying considerably, however, between different rock types. Dissolution of minerals from the bedrock and the high stability of the solution increase the overall salts concentration of bedrock groundwater to a level fivefold greater than that observed in soil groundwater. Electrical conductivity and alkalinity also were lower in aquifers situated in regions with coarse-grained soil types.

The concentrations of *calcium*, *magnesium*, *sodium* and *potassium* did not in general change significantly in the groundwater in comparison with the concentrations in infiltration water, although the mean sodium concentration in groundwater was double that in infiltration water and that of calcium slightly decreased. The relative changes in the concentrations of these ions are affected by different ion-exchange activities in the soil — water system. For example the mobilization of sodium and magnesium also in infiltration water is considerable, whereas calcium is rather efficiently adsorbed by soil particles (e.g. Beckett 1964).

The concentrations of calcium at the groundwater stations varied between 0.1 and 61 mg l^{-1} (mean 4.5 mg l^{-1} and median 2.9 mg l^{-1}. Magnesium concentrations were 0.1—27 mg l^{-1} (mean 1.5 mg l^{-1} and median 0.9 mg l^{-1}, sodium concentrations were 0.6—16 mg l^{-1} (mean 2.7 mg l^{-1} and median 2.2 mg l^{-1}) and those of potassium were 0.1—13 mg l^{-1} (mean 1.2 mg l^{-1} and median 0.8 mg l^{-1}).

The relative mean concentrations of the different metal ions of this group with respect to magnesium were:

$$Mg > 0.8\ K < 2.1\ Na < 3.1\ Ca \qquad (40)$$

Nitrate and *ammonium* were the most important nitrogen compounds in the groundwater. Variations in nitrate concentrations between the groundwater stations were considerable, 1.0—7600 $\mu g\ l^{-1}$ (mean 190 $\mu g\ l^{-1}$ and median 37 $\mu g\ l^{-1}$). Ammonium concentrations also showed wide variation, between 1.0 and 970 $\mu g\ l^{-1}$ (mean 40 $\mu g\ l^{-1}$ and median 9 $\mu g\ l^{-1}$). In a bedrock groundwater investigation conducted by Rönkä (1983) the mean concentration of nitrate was 1500 $\mu g\ l^{-1}$.

Nitrate does not usually create problems in the raw water of groundwater utilities. In 1977 the median concentration of nitrate in the raw water supply of small water supply plants (< 1500 $m^3\ d^{-1}$) was 850 $\mu g\ l^{-1}$ and in the supply of large plants (> 1500 $m^3\ d^{-1}$) the corresponding concentration was 1400 $\mu g\ l^{-1}$. In 1983 the mean nitrate concentration of all Finnish water supply plants was 1000 $\mu g\ l^{-1}$ (Vesihallitus 1984b).

However, the problem of nitrogen in groundwater often occurs in the water management of sparsely populated areas. Nitrate is usually a factor reducing the utilizability of the groundwater. For example Vainio (1984) reported that 26—33 % of samples from domestic wells in intensively fertilized regions of southern Finland contained levels of nitrate in excess of the maximum concentration of 30 mg l^{-1} recommended for drinking water by the public health authorities. The nitrate concentrations of water in wells were usually greatest after the spring thaw.

Since around 1950, the agricultural use of artificial fertilizers has increased enormously. The nitrates applied are only partly used by the crops, sometimes only 50 %, and the remainder is flushed away by rain and meltwater (Huisman 1981). According to some nitrogen balance calculations carried out in Sweden, about 42 % of added nitrogen in arable areas is leached into the soil and evaporated into the atmosphere (Brink 1981).

Ammonium is strongly adsorbed to soil particles and can be bound as complex compounds to humus (Hem 1972), whereas nitrate is very mobile. Ammonium is readily converted in the soil by nitrification to nitrite and nitrate. Nitrite is an unstable ion, which is oxidized biologically to nitrate at the early stages in infiltration. For this reason the concentrations of free nitrite in the soil are usually insignificant. Nitrogen does not occur to any significant extent in the minerals of the bedrock (Rönkä 1983).

In shallow aquifers nitrate is a rather stable form of nitrogen under aerobic conditions. In deep and also in anaerobic aquifers, in which the residence time of the groundwater is long, part of the nitrate is reduced. About 50 % of the nitrate of groundwater is released in gaseous form as a result of denitrification, which according to Steenvoorden (1976) different biochemical or chemical reactions:

biochemical: e.g. $5\ CH_3OH + 6\ NO_3^- \rightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^-$ (41)

chemical : e.g. $NO_3^- + 3\ H^+ + 2\ Fe^{2+} \rightarrow HNO_2 + 2\ Fe^{3+} + H_2O$ (42)

$$HNO_2 + H^+ + Fe^{2+} \rightarrow NO + Fe^{3+} + H_2O \qquad (43)$$

Englöv (1981) reported that nitrate is dinitrificated from groundwater under suitable conditions in Scandinavia. Nitrate may also be reduced and escape as nitrogen gas to the atmosphere from the root zone of the soil (Aslyng and Hansen 1982).

The mean nitrogen concentrations, Σ (NO_3 + NH_4), in groundwater was 230 μg l^{-1} at the groundwater observation stations. This was considerably lower than the corresponding mean in meltwater (736 μg l^{-1}) and infiltration water (585 μg l^{-1}). It therefore appears that significant denitrification also occurs in the conditions prevailing in groundwater in Finland, the nitrogen concentration in groundwater being only about 40 % of that in infiltration water.

Because nitrate reaches groundwater in small amounts relative to its loading and does not accumulate its influence on long-term groundwater acidification is less than that of sulfate (Harvey et al. 1981).

Concentrations of phosphate phosphorus varied between 1.0 and 370 μg l^{-1} (mean 15 μg l^{-1} and median 7 μg l^{-1}). The mean concentration in the groundwater was lower than that in meltwater (18 μg l^{-1}). The strong adsorption of phosphate to minerals and metal hydroxides and also its high biological activity are sufficient to explain the disappearance of phosphate during infiltration (Steenvoorden 1976).

Concentrations of *chloride* varied between 0.1 and 9.7 mg l^{-1} (mean 2.1 and median 1.6 mg l^{-1}). Chloride concentrations were slightly higher in groundwater than in infiltration water.

The concentrations increased as a result of evapotranspiration during summer and autumn-infiltration. According to Jacks (1978) the chloride of rainwater is concentrated threefold during its passage into groundwater. This estimate agrees rather well with the results of the present investigation, in which the enrichment coefficient of chloride between snow and groundwater was 2.6.

Chloride moves at the same rate as water and for this reason it is usually considered most suitable as an indicator of movements of water in the majority of soil types (Kurz and Melsted 1972).

The relatioship between the chloride concentrations of precipitation and groundwater can best be discerned in the shallow aquifers of the coastal region. In one study in Sweden a clear correlation was demonstrated between proximity of the sea and the chloride concentration of groundwater (Aastrup 1979).

Chloride concentrations usually increase with increasing depth of the groundwater. In very deep bedrock groundwater basins, concentrations of chloride may be over one thousand times greater than those observed in investigations of soil groundwater (e.g. Jacks 1973b, Jacobsen and Kelstrup 1981). In such deep basins the high chloride concentrations may be a hydrogeological relic from an earlier marine phase, or in coastal areas the reason may be intrusion of the sea water in more recent times.

In Finnish bedrock the average chloride content is 21 mg l^{-1} (Rönkä 1983), which is tenfold higher than in soil groundwater. The water contained in mafic rocks has nearly twice as high a chloride content as the water contained in felsic plutonic rocks.

The highest chloride concentrations were observed in the groundwater stations of coastal areas and the smallest correspondingly in eastern Finland. In northern Finland the concentration was higher than in other parts of the country. In Finland, as in Sweden, the chloride concentration of groundwater is affected mainly by the proximity of the sea spray (Aastrup 1979). The relic effect of the Littorina sea on chloride concentrations is only slight in shallow coarsely structured aquifers. The high chloride concentration (mean 27 mg l^{-1}) in the groundwater station of Kalajoki (40) is probably a result of intrusion of sea water.

The concentration of *sulfate* varied between 0.1 and 98 mg l^{-1} (mean 6.1 mg l^{-1} and median 3.4 mg l^{-1}). This level was slightly lower than that in infiltration water.

Sulfur is a biogenic element, which is readily accumulated into organic material. Sulfate may also be reduced by microbiological activity, as a result of which it usually degrades to hydrogen sulfide, which in turn may react e.g. with iron to form iron sulfides (Postma 1980).

The sulfate concentrations of groundwater were clearly lower in northern Finland than in the south of the country. These differences in concentration result partly from regional sulfate depositions. The regional differences are also affected in different bedrock regions e.g. by oxidization of pyrites, which has been shown to increase the sulfate concentration of groundwater in Norway (Englund and Myhrstad 1980).

In the coastal area of sulfide rich Littorina clay and mud deposits of Ostrobothnia the sulfate concentrations of groundwater are high. For example the maximum sulfate concentrations in Kälviä (39) and Laihia (31) were exceptionally high at 71 and 98 mg l^{-1}, respectively. The general level of sulfate concentrations was over tenfold in the sulfide regions compared with the level for the remainder of the country.

The concentrations of most ions (e.g. SO_4, Cl, Na, K, Ca and Mg) were usually greater in fine-

grained aquifers, due to the fact that the solubility effect of minerals always increases with decreasing hydraulic conductivity.

The *copper* concentrations of groundwater were between 0.1 and 100 $\mu g\ l^{-1}$ (mean 7.5 $\mu g\ l^{-1}$ and median 3 $\mu g\ l^{-1}$). The mean concentration level was lower in the groundwater than in the meltwater and infiltration water. In shallow aquifers, deposition of copper from the atmosphere usually has a greater effect on groundwater copper concentrations than dissolution from mineral rock types. In black schist regions and in deep bedrock groundwater basins, however, the effect of dissolution of sulfate concentrations is often greater than that of deposition from the atmosphere (Hyyppä 1981 and Rönkä 1983).

Concentrations of *lead* were between 0.1 and 80 $\mu g\ l^{-1}$ (mean 3.7 $\mu g\ l^{-1}$ and median 0.5 $\mu g\ l^{-1}$). The lead concentrations of groundwater were considerably lower than those of meltwater and infiltration water. The mechanism of transportation of lead through the soil is very similar to that of copper. Both are slowly removed from the solution by adsorption to soil humus during percolation, with the result that concentrations decrease with increasing depth (Bergkvist 1980). Lead is adsorbed by humus colloids and colloidal mineral particles more strongly than copper (Matthess 1982), which helps to explain the changes in the relationship between lead and copper concentrations in the groundwater after infiltration.

Concentration of *zinc* varied between 0.1 and 370 $\mu g\ l^{-1}$ (mean 12.9 $\mu g\ l^{-1}$ and median 4.0 $\mu g\ l^{-1}$). The median concentration in groundwater was about half that in meltwater, indicating the atmospheric origin of the zinc in groundwater. Zinc concentrations were not analyzed from infiltration water samples, because of zinc contamination of lysimeter vessels.

The highest levels of zinc in Finland are found in sulfide ore and black schist regions. The National Board of Waters has investigated water quality at its running-water stations since about 1962 (Laaksonen 1975). The highest zinc concentrations have been recorded in central Ostrobothnia, in the watercourse of the river Kokemäenjoki and in southwestern parts of the country. The highest mean concentrations varied in these regions between 73 $\mu g\ l^{-1}$ and 120 $\mu g\ l^{-1}$ (Mäkinen 1980). Niemi (1976) observed high zinc concentrations in the river Kälviänjoki (max 193 $\mu g\ l^{-1}$).

By comparison, the median zinc concentration of groundwater at the Kälviä groundwater station was 20 $\mu g\ l^{-1}$ (max 70 $\mu g\ l^{-1}$), which was clearly higher than the mean concentration in Finland.

Concentrations of *manganese* were between < 1 and 1800 $\mu g\ l^{-1}$ (mean 87 $\mu g\ l^{-1}$ and median 12 $\mu g\ l^{-1}$). The median concentration of manganese in the groundwater was lower than in the meltwater and infiltration water. Manganese usually has a tendency to precipitate in well oxygenated conditions as oxyhydrates, also due to the action of bacteria. This process already occurs in the unsaturated zone of the soil. The oxidization and precipitation of manganese occurs in a similar manner to that of iron and the precipitates are usually found in the same strata (Koljonen et al. 1976).

Concentrations of *aluminium* varied between < 0.5 and 6500 $\mu g\ l^{-1}$ (mean 215 $\mu g\ l^{-1}$ and median 50 $\mu g\ l^{-1}$). The median aluminium concentration of groundwater was the same as that of infiltration water and clearly higher than that of meltwater. The aluminium concentration of groundwater is determined mainly by the weathering and leaching of aluminium silicates in the soil. Increase in the aluminium concentration of groundwater is often a result of acidification of the soil due to acid deposition. The contribution of atmospheric sources to aluminium concentrations is negligible.

The following relationship between the metals discussed above was obtained in groundwater on the basis of median concentrations:

$$Pb < 6\ Cu < 9\ Zn < 26\ Mn < 100\ Al \qquad (44)$$

In comparison with the corresponding concentration relationships in meltwater and infiltration water the relative proportion of lead and manganese and to some extent also of copper and zinc decreased in groundwater, whereas the concentration of aluminium increased. The changes in relative concentrations partly explain their atmophilic or lithophilic origin in groundwater.

Elements (e.g. Hg, Cu, Cd, Zn and Pb) are termed atmophilic when their mass transport through the atmosphere is greater than that in streams. Elements such as aluminium, on the other hand, are termed lithophilic because their mass transport to the oceans by streams exceeds their transport through the atmosphere (Stumm and Morgan 1981).

The copper, lead and zinc concentrations of groundwater were rather similar in different soil-type regions and the solubility differences of these heavy metals due to soil type were therefore also small. This supports the conclusion reached earlier that the origin of these metals in the groundwater of shallow aquifers is mainly atmophilic, whereas aluminium, manganese and fluoride are lithophilic.

Cumulative distribution of concentration for

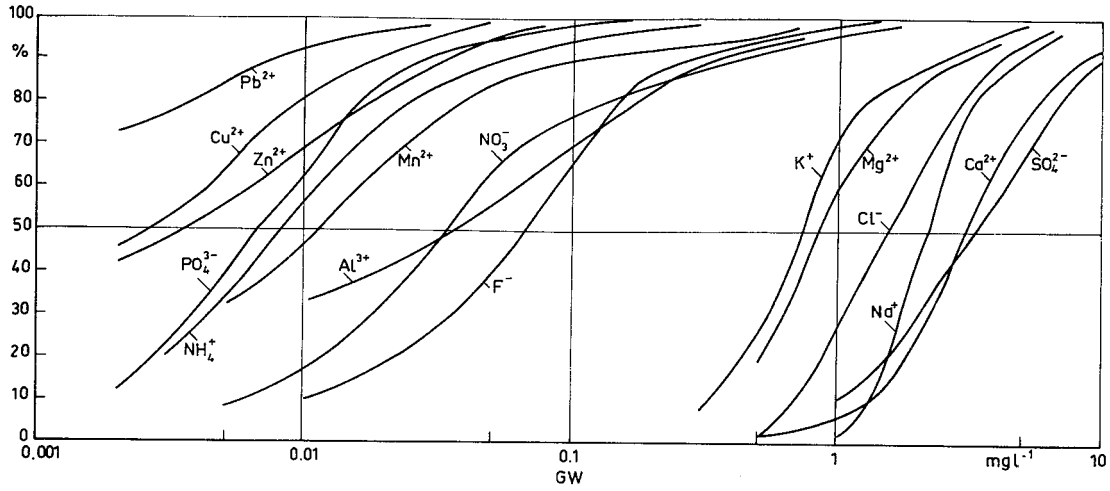

Fig. 19. Cumulative distribution of concentration for various constituents of groundwater at groundwater stations during the years 1976–1981.

various constituents of groundwater at groundwater stations during the years 1976—1981 are given in Fig. 19. The relationships between the mean concentrations of cations and anions of whole data were:

$$SO_4 > Ca > Na > Cl > Mg > K > F > NO_3 \approx Al > Mn > NH_4 > PO_4 > Zn > Cu > Pb \quad (45)$$

5.11 Concentration pattern

The usual statistical parameters of the pH, electrical conductivity and elemental concentrations of groundwater are presented in Table 23.

The interdependence of elemental concentrations in groundwater were investigated with the aid of a correlation matrix (Table 24). Regression functions were then calculated for the data pairs with the strongest correlations (r_3). r_1 and r_2 are corresponding correlation coefficients for the data pairs in the meltwater and in the infiltration water.

		r_3	(r_2)	(r_1)	
γ_{25}	$= 11.9 \cdot Alk + 2.3$	0.78***	—	—	(46)
γ_{25}	$= 0.8 \cdot Ca + 2.0$	0.88***	(0.74***)	(0.23***)	(47)
γ_{25}	$= 2.0 \cdot Mg + 2.9$	0.78***	(0.54***)	(0.01)	(48)
γ_{25}	$= 0.3 \cdot SO_4 + 3.7$	0.67***	(0.66***)	(0.70***)	(49)
Alk.	$= 0.1 \cdot Mg + 1.1$	0.74***	—	—	(50)
Alk.	$= 0.1 \cdot Ca + 0.04$	0.81***	—	—	(51)
Cl	$= 0.3 \cdot Na + 1.1$	0.42***	(0.48***)	(0.53***)	(52)
$PO_4 - P$	$= 11.2 \cdot K + 1.7$	0.57***	(−0.23)	0.47***	(53)
$NO_3 - N$	$= 300 \cdot K - 157$	0.76***	(0.14)	0.22***	(54)

Table 23. Groundwater analysis results at the groundwater stations during the period 1975—1981 (see list of symbols).

Parameter	Unit	n	min	max	mean	median	S	$S_{\bar{x}}$	$S/\bar{x}$
pH		2382	4.5	8.8	6.32	6.30	.56	0.02	0.09
γ_{25}	mS m^{-1}	2329	0.2	53	6.0	4.1	5.85	0.12	0.97
Alk.	mmol l^{-1}	2318	<0.01	4.8	0.31	0.22	0.37	0.01	1.22
SO_4	mg l^{-1}	2170	<0.1	98	6.1	3.4	10.6	0.23	1.7
Cl	mg l^{-1}	2286	<0.4	9.7	2.1	1.6	1.5	0.03	0.7
Na	mg l^{-1}	2225	0.6	16	2.7	2.2	1.8	0.04	0.7
K	mg l^{-1}	2195	<0.1	13	1.2	0.8	1.4	0.03	1.2
Ca	mg l^{-1}	2170	<0.1	61	4.5	2.9	5.7	0.12	1.3
Mg	mg l^{-1}	2220	0.1	27	1.4	0.9	2.1	0.04	1.4
NO_3–N	µg l^{-1}	2180	<1.0	7600	190	37	584	12.5	3.1
NH_4–N	µg l^{-1}	2219	<1.0	970	32.7	9	94	2.0	2.9
PO_4–P	µg l^{-1}	2228	<1.0	370	15.4	7	30	0.6	2.0
Cu	µg l^{-1}	2033	0.1	100	7.5	3	12.5	0.3	1.7
Mn	µg l^{-1}	2126	<1.0	1800	66.9	12	180	3.9	2.7
Pb	µg l^{-1}	2009	0.1	80	3.7	0.5	8.3	0.19	2.3
Zn	µg l^{-1}	2034	0.1	370	12.9	4.0	26.4	0.59	2.1
Al	µg l^{-1}	1054	<1.0	6500	215	50	708	21.8	3.3
F	µg l^{-1}	1190	<1.0	2700	160	70	314	9.1	2.0

Table 24. Correlation matrix for selected groundwater quality parameters.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.78***	1.00																
pH	0.25***	0.40***	1.00															
NO_3–N	0.26***	0.07	0.02	1.00														
NH_4–N	0.40***	0.16***	0.17***	0.04	1.00													
PO_4–P	0.45***	0.27***	0.03	0.21***	0.33***	1.00												
Cl	0.44***	0.20***	0.15***	0.41***	0.14***	0.22***	1.00											
Mn	0.58***	0.33***	0.05	0.05	0.56***	0.37***	0.16***	1.00										
Al	0.06	0.00	0.19***	0.04	0.16***	0.16***	0.00	0.33***	1.00									
F	0.15***	0.53***	0.11**	0.04	0.05	0.00	0.23***	0.22***	0.31***	1.00								
K	0.58***	0.29***	0.02	0.76***	0.26***	0.57***	0.43***	0.28***	0.07	0.01	1.00							
Ca	0.88***	0.81***	0.36***	0.11**	0.28***	0.36***	0.30***	0.52***	0.00	0.12***	0.40***	1.00						
Cu	0.02	0.04	0.26***	0.01	0.14***	0.14***	0.07	0.11**	0.24***	0.04	0.10**	0.04	1.00					
Pb	0.20***	0.12***	0.43***	0.06	0.22***	0.20***	0.03	0.46***	0.33***	0.06	0.16***	0.18***	0.43***	1.00				
Mg	0.78***	0.74***	0.09	0.09	0.38***	0.37***	0.30***	0.46***	0.11**	0.09	0.40***	0.72***	0.04	0.11**	1.00			
Na	0.63***	0.50***	0.10**	0.29***	0.20***	0.33***	0.42***	0.49***	0.25***	0.32***	0.46***	0.42***	0.09	0.34***	0.46***	1.00		
Zn	0.24***	0.06	0.15***	0.61***	0.16***	0.33***	0.19***	0.15***	0.17***	0.07	0.63***	0.09	0.29***	0.27***	0.11**	0.31***	1.00	
SO_4	0.67***	0.25***	0.05	0.10**	0.57***	0.39***	0.29***	0.70***	0.11**	0.15***	0.41***	0.55***	0.06	0.27***	0.41***	0.40***	0.21***	1.00

The correlations between elemental concentrations in groundwater (r_3) did not change significantly in comparison with those in the infiltration water (r_2), because the balance of elements in groundwater is largely determined during infiltration. On the other hand the correlations in the groundwater were often very different from those in snow (r_1).

Alkali and earthalkali metals have the greatest effect of cations on the total electrolyte concentration of groundwater. The correlation of calcium 0.88*** and magnesium 0.78*** with electrical conductivity was highly significant. Calcium correlated more closely with alkalinity 0.81*** than with pH 0.40***. The effect of calcium on groundwater pH is generally rather small in Finnish conditions. The correlation of potassium was highest with nitrate 0.76*** and phosphate 0.57***, which indicates the effects of the utilization of fertilizers.

The correlation between sodium and chloride 0.42*** did not change in the groundwater in comparison with the correlations in meltwater and infiltration water, indicating the relatively free movement of these rather unreactive ions between the atmosphere and the soil.

The best correlation coefficients involving the different metals were between aluminium and manganese 0.33***, copper and pH −0.26***, lead and manganese 0.46***, aluminium 0.33***, zinc and nitrate 0.61***, lead and pH −0.43*** and zinc and electrical conductivity 0.24***.

The correlations between metal concentrations vary considerably according to regional factors depending on e.g. the conditions of groundwater formation, the deposition of metals from the air and the regional mineralogy of the bedrock. The effects of geological factors on the quality of groundwater are investigated in more detail in sections 5.21 and 5.22.

5.2 Hydrogeological quality changes

"The chemical quality of water in many shallow aquifers exhibits cyclic variations that have seldom been noticed, rarely reported and apparently never described in detail." Pettyjohn (1976).

Few attempts have been made to determine the reasons for changes in substance concentrations of groundwater. It is generally believed that the quality of groundwater is rather constant. However, the processes by which groundwater is generated have many and considerable effects on its materials balance.

Cyclic changes in groundwater quality can be observed most clearly and most rapidly in shallow aquifers, in which concentration changes are often associated with the processes producing groundwater. In deep aquifers quality changes are usually slower and less extensive than in shallow aquifers.

Hackbarth (1981) recognized an annual pattern of variation in the chemistry of shallow groundwater in Canada. Concentrations of calcium, magnesium and bicarbonate reached their lowest annual values in the spring and increased rapidly by early summer. The concentrations of these ions gradually decreased during the autumn and winter. This cycle is related to the abundance of dissolved carbon dioxide in the recharge water.

Spring and autumn are typically times of the highest sulfate concentrations in Canada. This pattern is coincident with recharge events and is related to leaching of sulfur compounds. High chloride concentration during the winter is related to slower rates of groundwater flow and the consequent increased opportunity for release of ions from chloride-bearing minerals.

Within the groundwater network of the Geological Survey of Sweden, the chemical composition of groundwater has been monitored during the past 15 years. Time series from many stations has revealed changes in the contents of magnesium, calcium, sulfate and chloride. At some stations changes also occurred in the sodium, nitrate or hydrocarbonate contents, while very few stations showed changes in potassium or pH.

Some of the changes have been interpreted as being caused by changes in land use or by the use of fertilizers, while others were probably due to climatic variations. The increased contents of magnesium and calcium were probably caused by environmental acidification and weathering processes, particularly in southern Sweden. (Aastrup and Persson 1984). For the main part, the adverse effects of groundwater quality are the result of man's activity at the ground surface, unintentionally by agriculture and industry.

5.21 Changes in different soil types

The mean and median concentrations in groundwater were examined for different soil types on the basis of the classification presented in Section 2.1.

A Coarse-grained sand and gravel regions (22 groundwater stations)
B Fine-grained silts and clays (7 groundwater stations)
C Gravelly, sandy and silty tills (25 groundwater stations)

Table 25. Mean ($\bar{x}$) and median (Md) concentrations in groundwater and their standard deviations (S) in different groups of soil types. A coarse-grained soils (n = 850); B fine-grained soils (n = 250); C moraines (n = 1200); D whole data.

Parameter	Unit	A			B			C			D		
		$\bar{x}$	Md	S	$\bar{x}$	Md	S	$\bar{x}$	Md	S	$\bar{x}$	Md	S
pH		—	6.2	0.7	—	6.6	0.4	—	6.3	0.4	—	6.3	0.6
γ_{25}	mS m^{-1}	4.1	3.0	3.1	9.5	6.2	8.6	6.8	5.2	6.4	6.0	4.1	0.6
Alk	mmol l^{-1}	0.2	0.2	0.2	0.4	0.3	0.4	0.4	0.3	0.4	0.3	0.2	0.4
SO_4	mg l^{-1}	3.3	3.0	2.2	13	6	19	6.7	3.7	11.2	6.1	3.4	10.6
Cl	mg l^{-1}	1.4	1.2	0.7	3.8	3.1	1.9	2.2	1.7	1.5	2.1	1.6	1.5
Na	mg l^{-1}	2.0	1.8	1.5	3.2	2.8	1.2	3.1	2.6	1.9	2.7	2.2	1.8
K	mg l^{-1}	0.7	0.6	0.4	1.7	1.4	1.2	1.4	0.8	1.8	1.2	0.8	1.4
Ca	mg l^{-1}	3.1	2.3	2.9	8.3	4.3	10	4.9	3.6	5.5	4.5	2.9	5.7
Mg	mg l^{-1}	0.7	0.6	0.4	1.6	1.3	1.2	1.9	1.1	2.7	1.4	0.9	2.1
NO_3–N	μg l^{-1}	59	24	102	443	60	601	233	57	739	190	37	578
NH_4–N	μg l^{-1}	16	8	22	37	8	102	44	9	119	33	9	96
PO_4–P	μg l^{-1}	9.9	6.0	11	19	7	36	19	7	37	15	7	30
Cu	μg l^{-1}	8.0	2.0	14	4.2	2.0	5	7.9	4.0	12	7.5	3.0	12
Mn	μg l^{-1}	18	10	23	166	7	362	81	15	173	67	12	177
Pb	μg l^{-1}	3.6	0.5	9	4.3	0.5	10	3.6	0.5	7	3.7	0.5	8
Zn	μg l^{-1}	9.4	3.0	15	6.8	3.0	10	17	5.0	34	13	4	26
Al	μg l^{-1}	124	50	329	70	30	136	320	50	951	215	50	711
F	μg l^{-1}	65	50	56	157	95	132	237	85	425	160	70	314

The permeability of the soil, which determines the time used for infiltration between snowmelt and groundwater recharge, has the greatest effect on concentration differences in the groundwater of different soil-type regions. The finer the soil structure and the longer the infiltration period, the more do soil processes alter the quality of the infiltrating water and thus affect the final composition of the groundwater (Table 25).

The influence of atmospheric impurities on groundwater quality is greatest in regions with coarse-grained soil. The effects of acidic meltwaters were also most obvious in the groundwater of sandy and gravelly soils, where the median of pH (6.2) was lower than in the moraines (median 6.3) and in the fine soil types (median 6.6).

The greater the retention time of the groundwater in the soil and bedrock, the greater is the effect of alkaline components, on the pH balance of the water, even in regions with acidic bedrock types. For example at the Oripää groundwater station, where the prevailing bedrock is granodiorite, the pH-median was 8.4. The artesian groundwater in the bordering region of the Oripää ridge is pressurized beneath clay lenses with the result that the retention time of the groundwater is long.

The standard deviations of the quality parameters of groundwater were usually smaller in regions with coarse-grained soils. In most cases the deviations increased with decrease in the particle size of the major soil type.

In addition to particle size of the soil, the thickness of the leaching zone of the groundwater also had a significant effect on the elemental concentrations of the groundwater. In this context the leaching zone is taken to be thickness of the zone between the extremes of variation in the level of the groundwater. The thickness of the leaching zone of groundwater varied between 40 and 288 cm at the groundwater stations of the National Board of Waters during the years 1975—1982. Annual variation in the level of groundwater is greater in areas with fine-grained soils and the leaching of the products of weathering is therefore also most efficient in such areas.

The correlations of some chosen material pairs in groundwater are examined in the following for different types of the soil (Tables 26—28).

In this way an estimate is made of the cause-effect relationship between the material concentrations of groundwater on the one hand and soil type and deposition of the other.

The correlations between concentrations in groundwater varied in different soil types. In coarse-grained soils the correlation of alkalinity, calcium and sodium with the pH of groundwater was considerably more significant than in the other soil types, although the mean pH value was lowest in this soil type. The correlation of copper with zinc and lead was also most significant in the coarse soils.

In fine-grained and morainic soils the correlations between the above metals were rather poor.

Table 26. Correlation matrix of the groundwater analyses in coarse-grained soil regions.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.91***	1.00																
pH	0.59***	0.70***	1.00															
NO_3–N	0.08*	0.02	0.07	1.00														
NH_4–N	0.07	0.16***	0.28***	0.02	1.00													
PO_4–P	0.25***	0.21***	0.10	0.06	0.20***	1.00												
Cl	0.49***	0.35***	0.33***	0.14***	0.03	0.20***	1.00											
Mn	0.06	0.05	0.23***	0.05	0.36***	0.23***	0.01	1.00										
Al	0.03	0.02	0.21***	0.07	0.16**	0.38***	0.19***	0.39***	1.00									
F	0.22***	0.24***	0.36***	0.04	0.11*	0.02	0.07	0.18***	0.13*	1.00								
K	0.47***	0.29***	0.06	0.02	0.09*	0.43***	0.27***	0.08*	0.04	0.01	1.00							
Ca	0.86***	0.84***	0.76***	0.13**	0.16***	0.15***	0.34***	0.08*	0.10	0.36***	0.25***	1.00						
Cu	0.03	0.07*	0.28***	0.06	0.30***	0.12***	0.10	0.18***	0.30***	0.04	0.28***	0.11	1.00					
Pb	0.19***	0.11**	0.19***	0.04	0.28***	0.33***	0.11**	0.26***	0.25***	0.04	0.49***	0.01	0.52***	1.00				
Mg	0.45***	0.46***	0.60***	0.11**	0.16***	0.17***	0.17***	0.13***	0.11*	0.20***	0.27***	0.53***	0.02	0.04	1.00			
Na	0.79***	0.74***	0.35***	0.02	0.02	0.28***	0.32***	0.08	0.08	0.09	0.40***	0.43***	0.04	0.36***	0.24***	1.00		
Zn	0.10**	0.03	0.29***	0.03	0.35***	0.18***	0.03	0.24***	0.27***	0.06	0.30***	0.08	0.62***	0.57***	0.12**	0.09*	1.00	
SO_4	0.68***	0.50***	0.30***	0.16***	0.03	0.20***	0.43***	0.06	0.14**	0.18***	0.34***	0.48***	0.06	0.24***	0.09*	0.54***	0.14***	1.00

Table 27. Correlation matrix of the groundwater analyses in fine-grained soil regions.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.91***	1.00																
pH	0.48***	0.54***	1.00															
NO_3–N	0.10	0.11	0.55***	1.00														
NH_4–N	0.62***	0.75***	0.36***	0.12	1.00													
PO_4–P	0.64***	0.54***	0.25***	0.15*	0.51***	1.00												
Cl	0.01	0.03	0.07	0.08	0.04	0.03	1.00											
Mn	0.80***	0.67***	0.46***	0.24***	0.48***	0.50***	0.07	1.00										
Al	0.35***	0.22*	0.16	0.02	0.29**	0.63***	0.03	0.52***	1.00									
F	0.34***	0.20*	0.30***	0.50***	0.12	0.35***	0.34***	0.39***	0.22*	1.00								
K	0.65***	0.58***	0.12	0.57***	0.36***	0.31***	0.00	0.44***	0.23*	0.13	1.00							
Ca	0.93***	0.84***	0.49***	0.17*	0.52***	0.58***	0.07	0.82***	0.44***	0.44***	0.58***	1.00						
Cu	0.14*	0.19**	0.19**	0.30***	0.11	0.02	0.17*	0.09	0.13	0.23*	0.41***	0.10	1.00					
Pb	0.57***	0.48***	0.32***	0.13	0.20**	0.30***	0.07	0.77***	0.39***	0.26**	0.47***	0.68***	0.18*	1.00				
Mg	0.90***	0.82***	0.29***	0.17*	0.56***	0.54***	0.17*	0.77***	0.43***	0.14	0.78***	0.85***	0.22**	0.58***	1.00			
Na	0.89***	0.75***	0.36***	0.06	0.48***	0.60***	0.01	0.82***	0.45***	0.44***	0.69***	0.90***	0.15*	0.69***	0.87***	1.00		
Zn	0.51***	0.56***	0.20**	0.11	0.48***	0.21**	0.17*	0.59***	0.35***	0.13	0.47***	0.54***	0.24***	0.58***	0.51***	0.54***	1.00	
SO_4	0.91***	0.80***	0.50***	0.22**	0.49***	0.61***	0.14*	0.87***	0.45***	0.51***	0.57***	0.96***	0.09	0.68***	0.83***	0.91***	0.53***	1.00

Table 28. Correlation matrix of the groundwater analyses in moraine soils.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.70***	1.00																
pH	0.02	0.29***	1.00															
NO_3–N	0.29***	0.07	0.02	1.00														
NH_4–N	0.38***	0.06	0.32***	0.06	1.00													
PO_4–P	0.40***	0.20***	0.14**	0.25***	0.30***	1.00												
Cl	0.48***	0.17***	0.01	0.44***	0.14**	0.25***	1.00											
Mn	0.45***	0.21***	0.33***	0.07	0.67***	0.31***	0.13**	1.00										
Al	0.06	0.01	0.26***	0.05	0.17***	0.13*	0.02	0.56***	1.00									
F	0.08	0.00	0.11*	0.05	0.02	0.07	0.31***	0.23***	0.31***	1.00								
K	0.55***	0.22***	0.09	0.79***	0.23***	0.61***	0.48***	0.21***	0.05	0.05	1.00							
Ca	0.88***	0.87***	0.20***	0.13***	0.26***	0.30***	0.32***	0.29***	0.01	0.06	0.37***	1.00						
Cu	0.06	0.03	0.22***	0.12***	0.17***	0.21***	0.00	0.25***	0.25***	0.07	0.11	0.02	1.00					
Pb	0.12*	0.03	0.21***	0.08	0.24***	0.17***	0.02	0.47***	0.47***	0.09	0.08	0.01	0.42***	1.00				
Mg	0.87***	0.80***	0.06	0.04	0.35***	0.35***	0.30***	0.48***	0.09	0.02	0.34***	0.88***	0.07	0.13	1.00			
Na	0.54***	0.37***	0.15***	0.33***	0.15**	0.29***	0.47***	0.50***	0.32***	0.31***	0.41***	0.32***	0.16***	0.34***	0.47***	1.00		
Zn	0.28***	0.03	0.12**	0.69***	0.13**	0.38***	0.31***	0.15**	0.14**	0.04	0.71***	0.10	0.22***	0.21***	0.09	0.35***	1.00	
SO_4	0.53***	0.03	0.43***	0.13***	0.69***	0.31***	0.33***	0.55***	0.14**	0.10	0.36***	0.27***	0.16***	0.16***	0.38***	0.32***	0.28***	1.00

Changes in relative concentrations in the fine-grained and morainic aquifers resulted from differential adsorption of the metals on soil particles. Leaching of metals was apparently rather small, because the metal concentrations did not increase significantly in the groundwater after infiltration.The concentrations of two metals with widespread occurrence in soil, namely manganese and aluminium, correlated best in fine-soil aquifers with the following ions: Mn/Na ($r = 0.82^{***}$), Mn/Ca ($r = 0.82^{***}$), Mn/Pb ($r = 0.77^{***}$), Al/SO_4 ($r = 0.45^{***}$), Al/Na ($r = 0.45^{***}$) and Al/Ca ($r = 0.44^{***}$). In addition, the concentration of sulfur was highly significantly correlated with those of calcium $r = 0.95^{***}$, sodium $r = 0.91^{***}$ and electrical conductivity $r = 0.91^{***}$.

The interdependences of these parameters are largely due to weathering of aluminium silicates and sulfide minerals in the aquifers of fine-grained soils. According to a comparison of correlations in coarse-grained aquifers, on the other hand, the effects of weathering on the materials balance of groundwater were rather slight in the latter soil type.

Temporal changes in the concentrations on some of the most abundant groundwater materials were examined in detail for the different soil types with the aid of some examples. The concentration changes were in the main monitored in conjunction with the spring melt.

Coarse-grained aquifers are represented by the groundwater stations of Oripää (7), Halsua (37), Alakangas (47) and Tullinkangas (4) (Figs. 20—23). The artesian groundwater at Oripää differs in its hydrography from the water at the other stations. Variations in the groundwater driving head are slight and irregular and do not represent any form of seasonal variation. On the other hand, very definite spring and autumn maximum and summer and winter minimum are characteristic of the groundwater at the Halsua and Tullinkangas stations. At Alakangas in gravel soil, the annual hydrological rhythm has only two phases, in which the spring and autumn maximum are joined and the winter minimum is rather long.

In many cases the concentrations of sulfate, calcium, magnesium, sodium and alkalinity of groundwater increase during or shortly after the spring thaw, causing an increase in water pH. The reaction of acidic meltwater in infiltration water and in groundwater results in neutralization, although the sulfate concentration of the groundwater often increases at the same time.

Chloride concentrations in groundwater also showed temporal variation. Concentrations in dry seasons e.g. in 1978 and 1979 at Halsua and Tullinkangas (Figs. 21 and 23), were often higher than in rainy periods. Increase in the concentration of chloride is caused during dry weather by greater concentration of meltwater in the soil due to evapotranspiration.

Changes in the quality parameters of the groundwater were usually greatest in those aquifers in which variations in the pietzometric level were greatest and most complex. At Alakangas (Fig. 22), where the annual variations were only 2-stage, the variations in concentrations were also smaller. The role of evaporation in the concentration of soil water is less important in the climatic conditions prevailing at this site than in southern Finland. This is illustrated by the low level of chloride concentration at Alakangas and by the small temporal variations.

Clear variations between the concentrations of different elements were also observed in the conditions of the artesian groundwater at Orivesi. The maximum concentrations of sulfate and alkalinity were often recorded at the end of the year.

In the till aquifers at Laihia (31) and Kullisuo (48) (Figs. 24 and 25) the concentrations of elements and their variations were usually greater than in coarse-grained aquifers. For example at the Laihia groundwater station, where the variations in groundwater height are in 4-stages, the effects of snowmelt and autumn rains were immediately apparent in the growth in concentrations of different elements.

The sulfate concentration in the Laihia sulfide rich soils is high and the pH of the groundwater is low. As a result of melting the water sulfate concentration and pH often further increase. Even in exceptionally acidic conditions the effects of alkaline factors of the pH-balance of groundwater are greater than the acidifying effect of H^+ and H_3O^+ ions.

At the Kullisuo groundwater station the annual variation in height of the groundwater level follows a 2-stage cycle as at Alakangas. For the same reason as at Alakangas, the variations in chloride concentration at Kullisuo are lower than those at e.g. Laihia. In the fine-grained aquifers at Viinikkala (22) and Vehkoo (34) (Figs. 26 and 27) the natural variations in groundwater level are both rapid and extensive, with the result that changes in substance concentrations are also greater and more rapid than in areas characterized by coarse-grained soils.

In fine-structured soil types the time lag between groundwater recharge and the transportation of most materials may be as long as several months, as estimated on the basis of the maximum

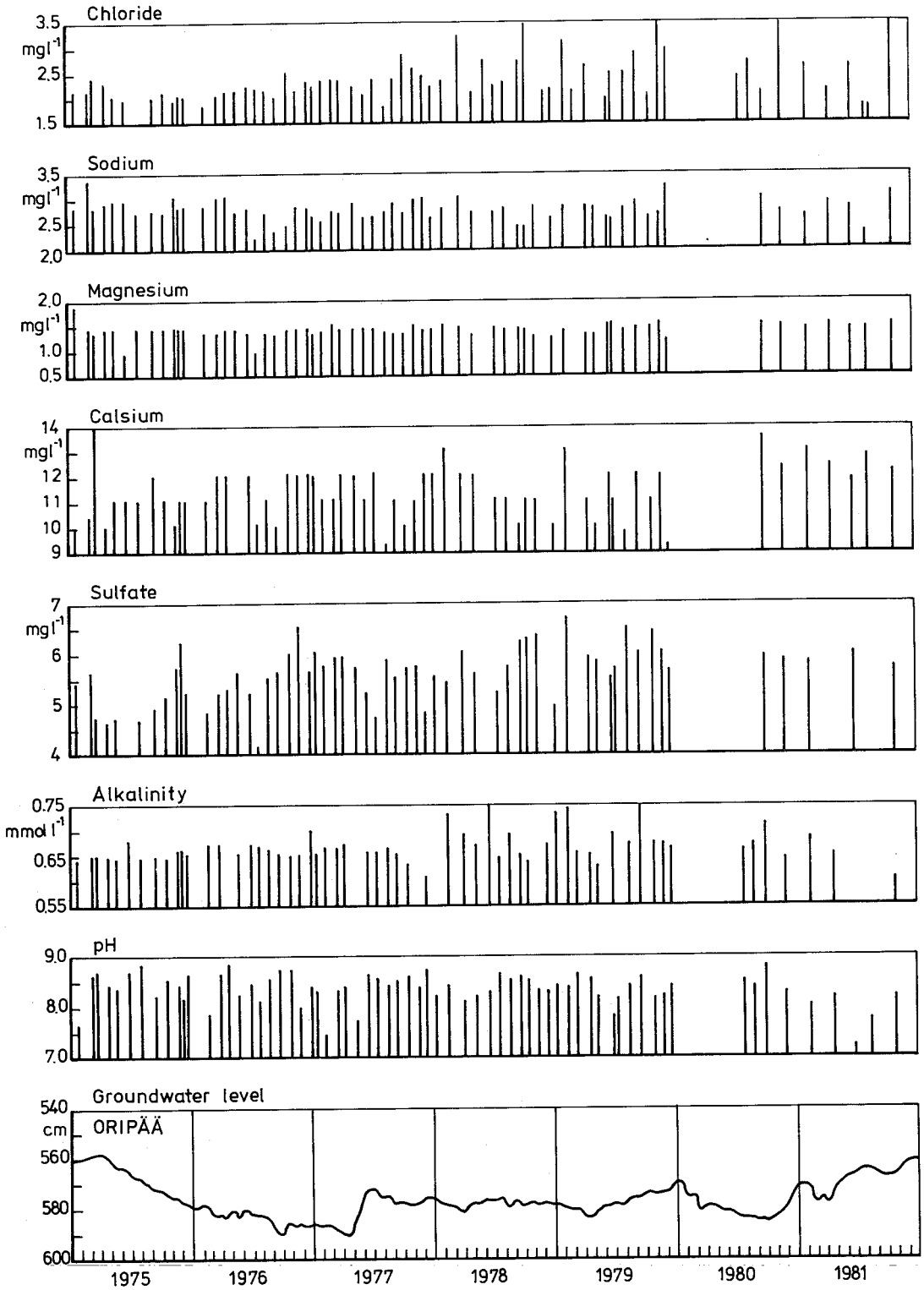

Fig. 20. Temporal changes in the concentrations of some groundwater substances at Oripää groundwater station.

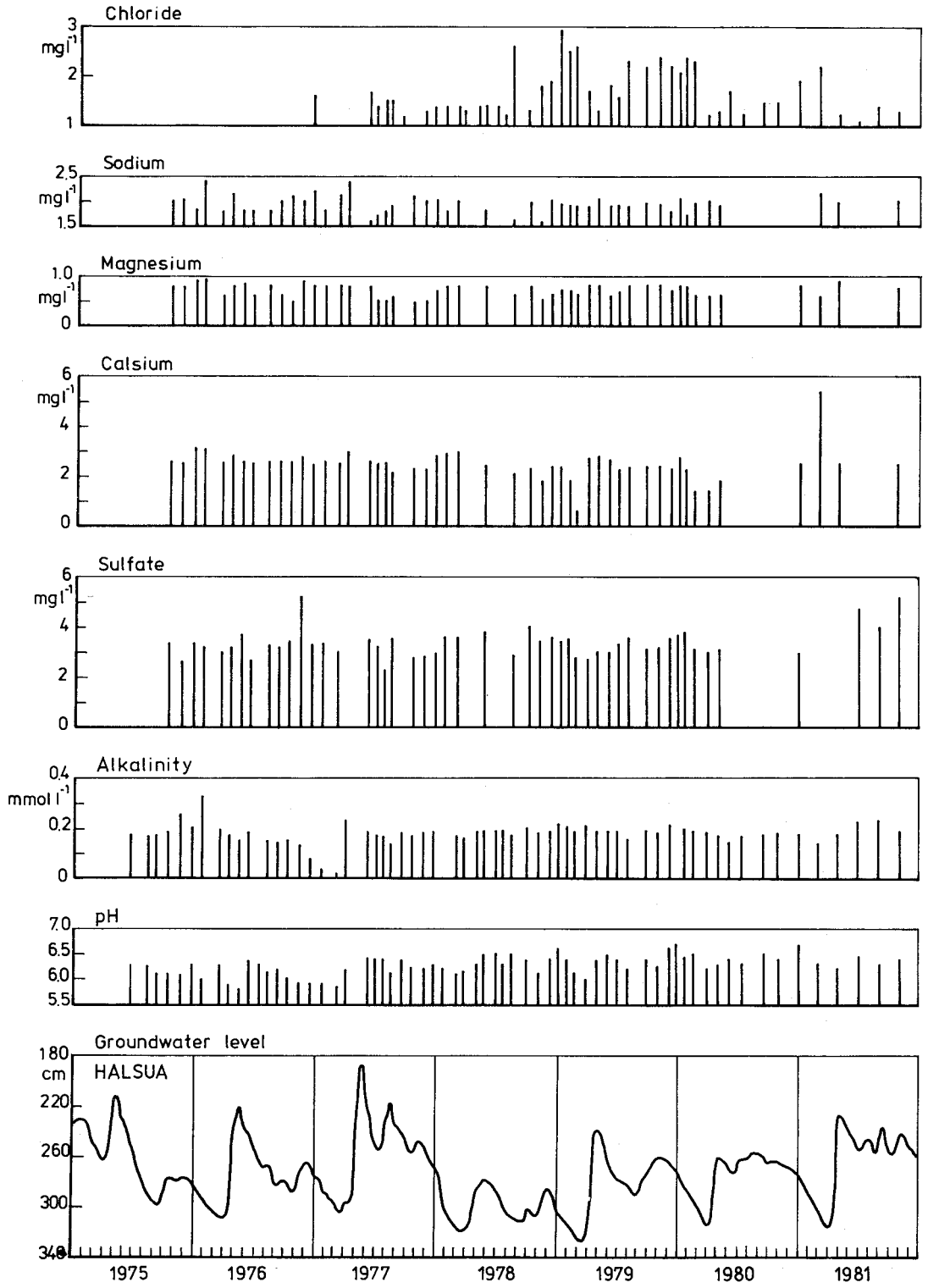

Fig. 21. Temporal changes in the concentrations of some groundwater substances at Halsua groundwater station.

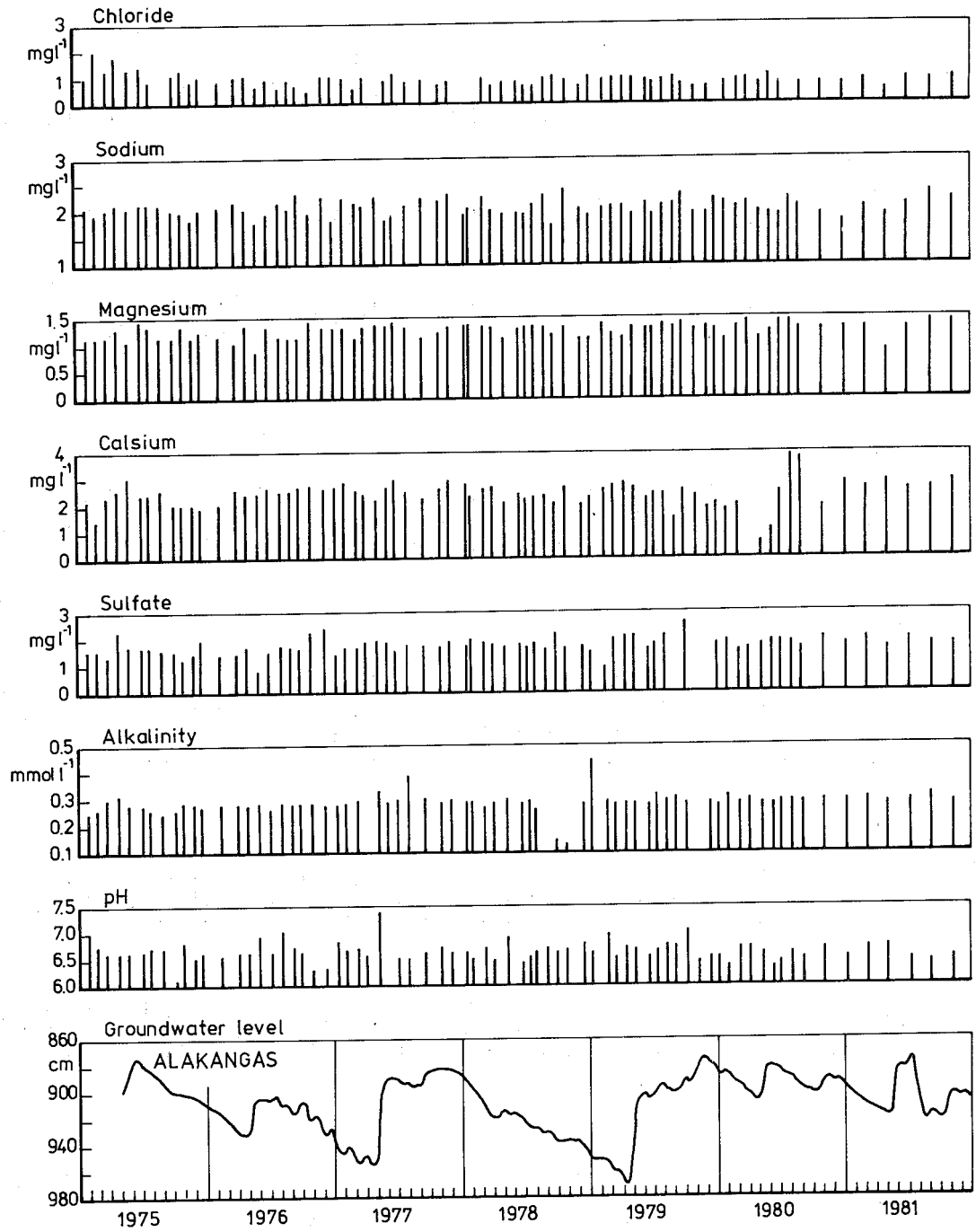

Fig. 22. Temporal changes in the concentrations of some groundwater substances at Alakangas groundwater station.

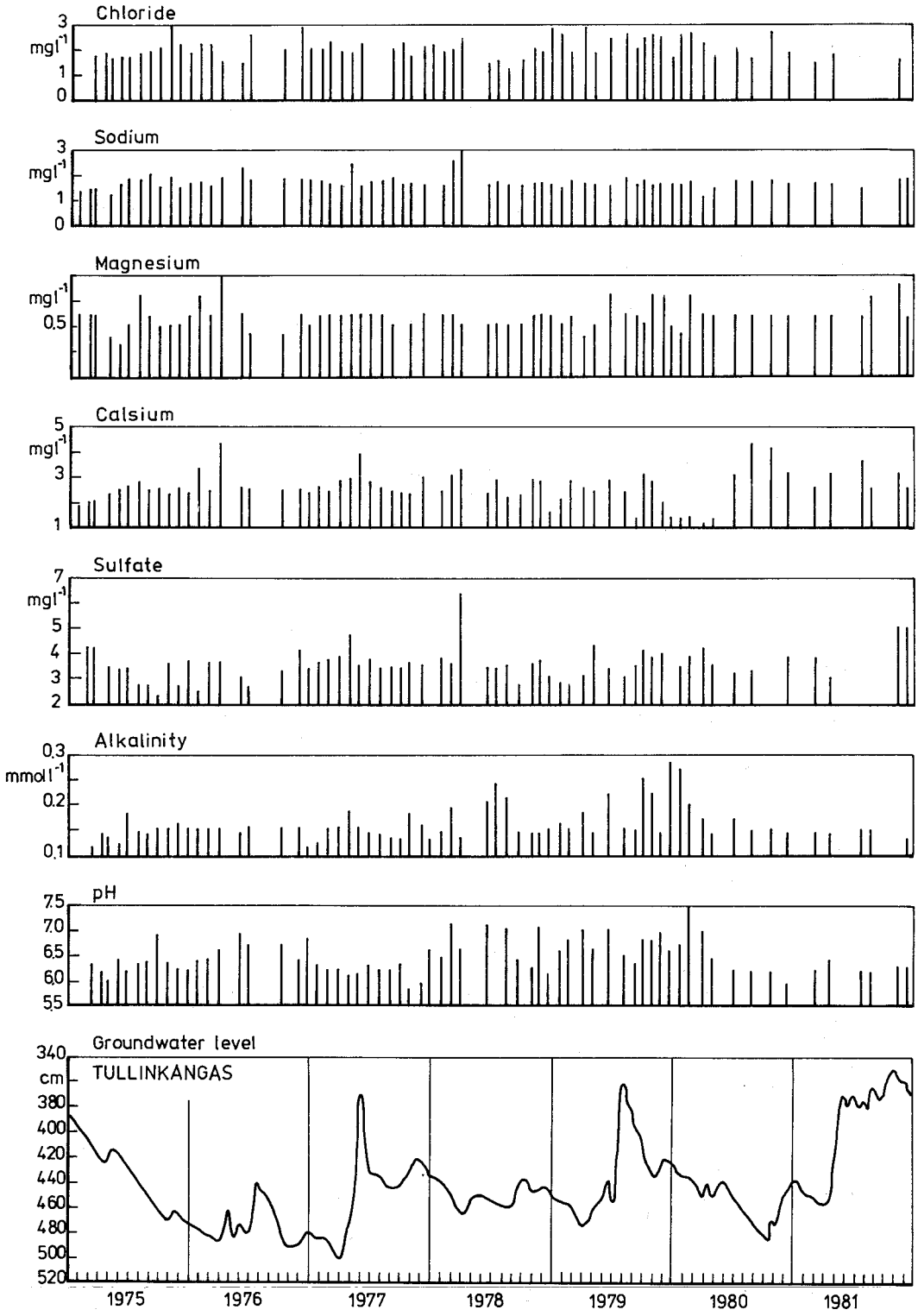

Fig. 23. Temporal changes in the concentrations of some groundwater substances at Tullinkangas groundwat- station.

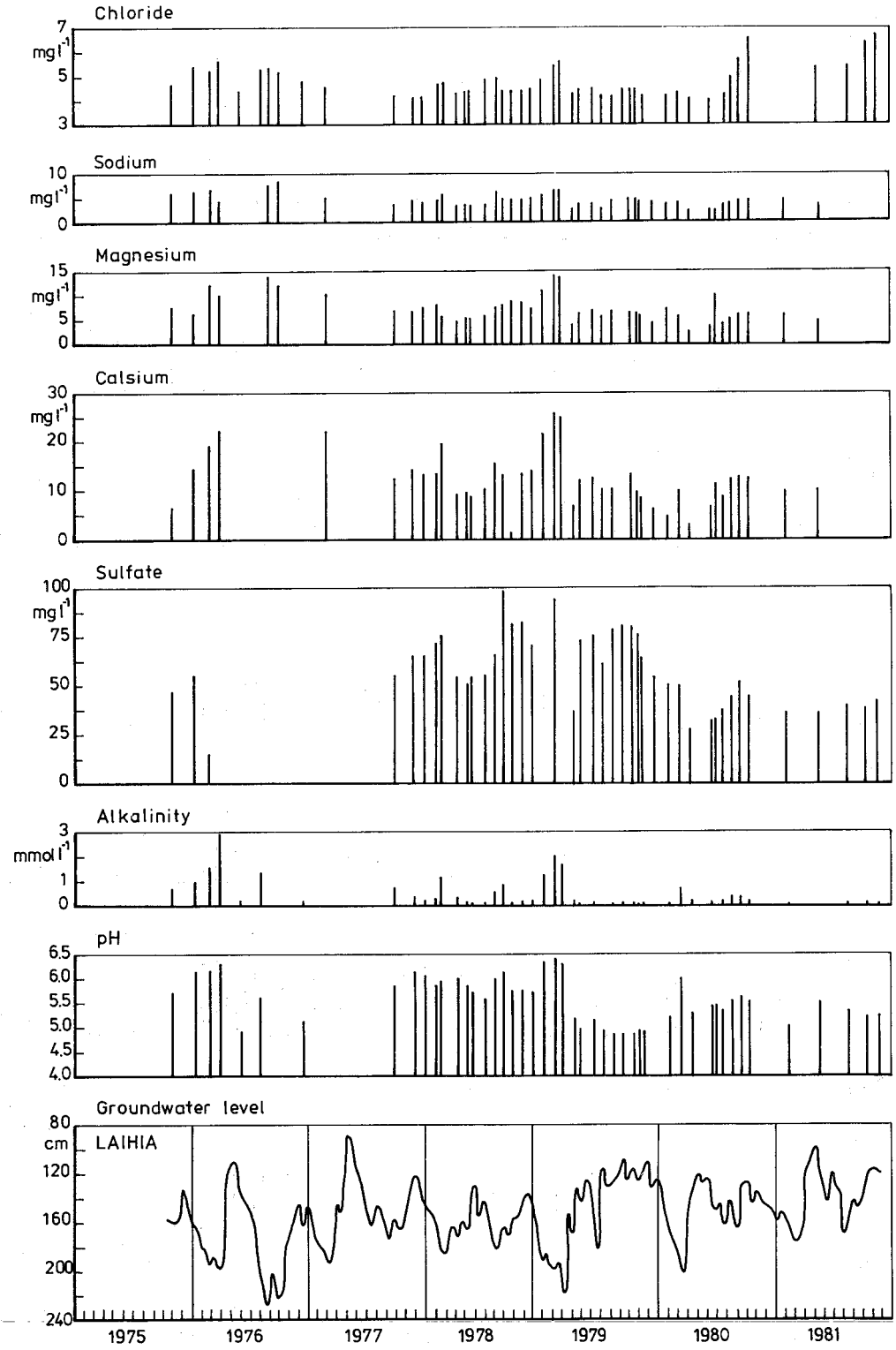

Fig. 24. Temporal changes in the concentrations of some groundwater substances at Laihia groundwater station.

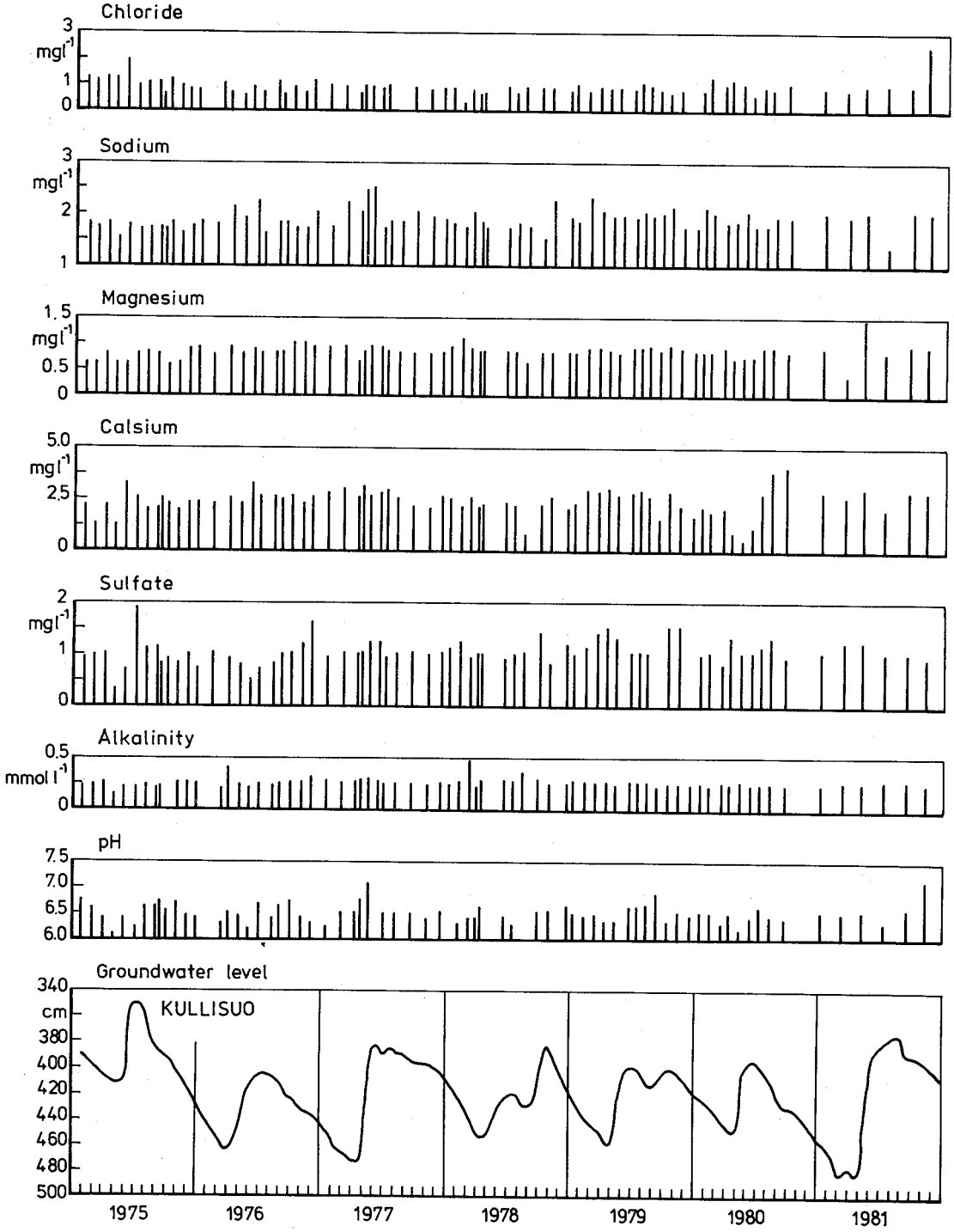

Fig. 25. Temporal changes in the concentrations of some groundwater substances at Kullisuo groundwater station.

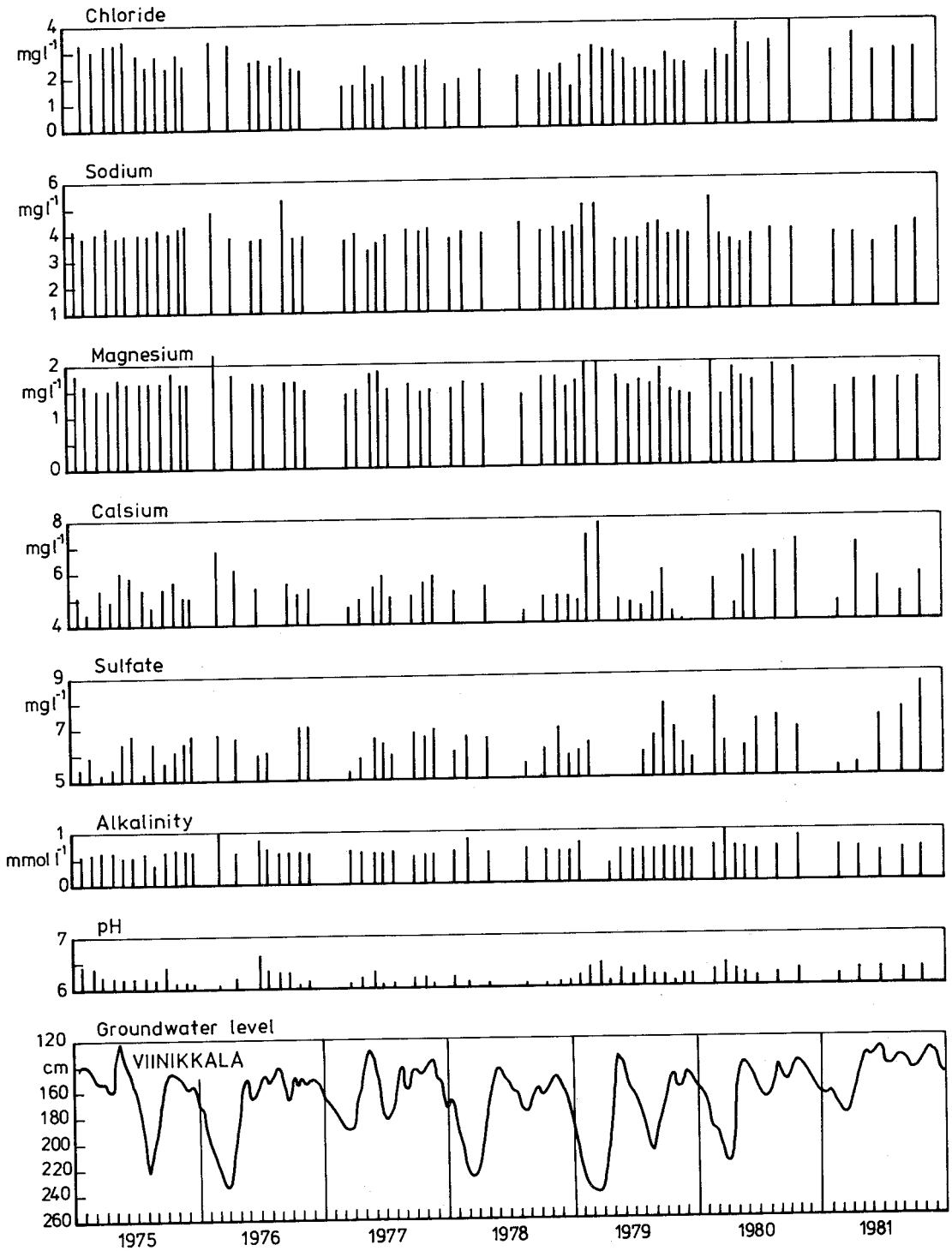

Fig. 26. Temporal changes in the concentrations of some groundwater substances at Viinikkala groundwater station.

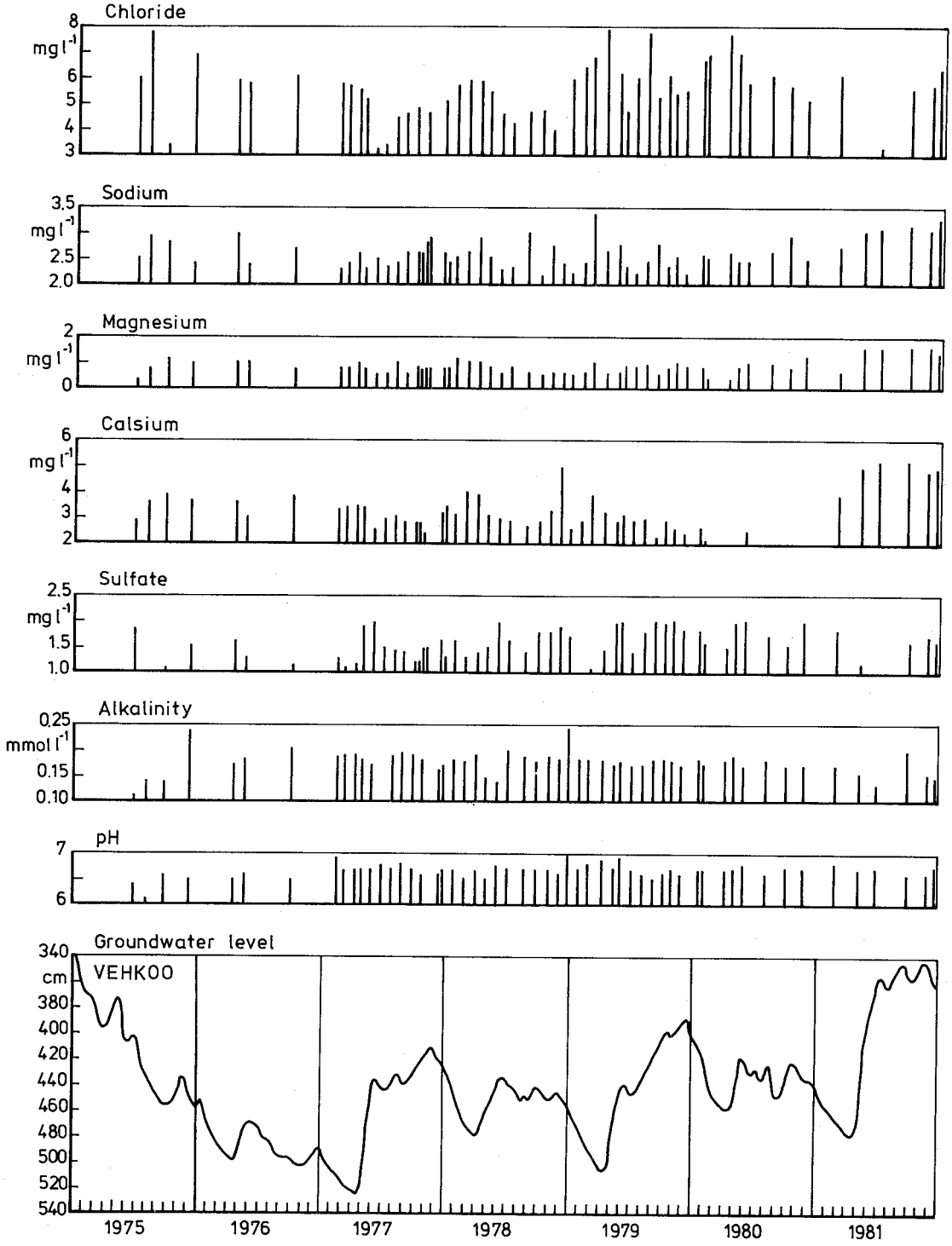

Fig. 27. Temporal changes in the concentrations of some groundwater substances at Vehkoo groundwater station.

of groundwater formation and material concentrations. For example at Viinikkala the pH and alkalinity maximum of groundwater often occur at the time of minimum groundwater level.

As a result of different infiltration rates the concentration of materials in the soil surface due to evaporation is more pronounced in regions with fine soil types than in coarse-grained soils. This also affects the elemental composition of groundwater, particularly in the case of elements (e.g. chlorine) with low reactivity in the soil (Fig. 26).

5.22 Changes in different kinds of crystalline bedrock

In shallow aquifers the immediate effect of bedrock type on groundwater quality is difficult to estimate. The mineralogy of the soil in the groundwater recharge area does not always correspond to that of the bedrock beneath the groundwater. However, the rock types examined in this work occurred over rather widespread areas and in unified zones with respect to the field areas, so that the mineral composition in the loose soil in the groundwater formation basin usually also corresponded rather closely with that of the bedrock. The effect of different rock types on groundwater quality was examined roughly in Table 29 on the basis of the rock classification presented in Section 2.1.

Statistically significant differences in groundwater quality constituents were recorded between the different bedrock groups. Concentrations were lower in areas with acidic, weathering-resistant rocks than in other areas. This could be seen clearly in electrical conductivity, alkalinity, sulfate, sodium, potassium, calcium, magnesium, nitrate, ammonium, phosphate, aluminium and the heavy metals. In regions with basic rock types the elemental concentrations of the groundwater were in most cases at a higher level, e.g. calcium and magnesium (Table 29).

In the group of rock types other than the two mentioned above the effect of rapakivi-granite on the fluoride concentration of groundwater was for example very clear. The fluoride content of groundwater in rapakivi-granite areas provides in Finnish conditions a clear demonstration of the direct solubility effect of the soil and bedrock type on groundwater. In the following the cause-effect relationship between the bedrock and the meltwater on the one hand and the fluoride concentration of groundwater on the other is examined.

Fluorine does not occur as a free ion in the environment, but is apt to join with other ions to form complexes with calcium and magnesium. Fluorine often occurs as fluorite (CaF_2) or fluorapatite ($Ca_5(PO_4)_3F$).

Fluorine is released into the groundwater during the weathering processes of minerals mainly in rapakivi areas. In areas characterized by basic rocks the fluorine of the groundwater is assumed to be of atmospheric origin, because the fluoride content of rain and snow varies on average between 50 and 250 $\mu g\ l^{-1}$ in Finland (Soveri and Soveri 1981).

The fluoride content of the Finnish bedrock is on average 0.08 % and in rapakivi-granite areas the concentration may even be to 0.5 % (Rankama and Sahama 1950). In the rapakivi areas of south-

Table 29. Mean concentrations and concentration ranges in groundwater in different bedrock groups at the groundwater stations in the National Board of Waters during the years 1975—1981.

Parameter	Unit	Felsic			Schists			Mafic			Miscellaneous		
		min	max	x̄	min	max	x̄	min	max	x̄	min	max	x̄
pH		4.5	8.8	—	4.5	8.6	—	4.8	6.6	—	5.4	7.5	—
γ_{25}	mS m^{-1}	1.3	12.0	4.6	0.2	53.0	7.1	5.8	5.90	13.8	4.0	16.0	7.3
Alk	mmol l^{-1}	<0.01	0.98	0.26	0.00	4.84	0.36	<0.01	2.92	0.33	0.02	1.40	0.39
SO_4	mg l^{-1}	0.1	13.0	3.5	0.1	71.0	7.6	5.1	98.0	27.9	1.1	16.0	7.1
Cl	mg l^{-1}	0.1	9.0	2.0	0.4	9.7	1.8	1.5	9.2	3.4	0.8	8.0	2.8
Na	mg l^{-1}	0.6	8.5	2.4	0.7	16.0	2.7	2.1	8.1	3.6	2.2	16.0	4.5
K	mg l^{-1}	0.1	4.1	0.8	<0.1	13.0	1.6	2.1	6.8	3.1	0.3	2.7	0.9
Ca	mg l^{-1}	0.1	14.0	3.5	0.1	61.0	5.6	1.3	26.0	8.2	2.1	8.8	5.4
Mg	mg l^{-1}	0.1	8.8	1.2	0.1	27.0	1.4	1.3	14.0	4.0	0.5	6.0	2.1
F	$\mu g\ l^{-1}$	<1	440	96	<1	570	72	1	500	157	<1	2700	918
Cu	$\mu g\ l^{-1}$	0.1	100	6	0.5	90	9	0.3	36	11	0.5	58	9
Mn	$\mu g\ l^{-1}$	<1	950	23	<1	1800	104	0	940	203	<1	890	141
Pb	$\mu g\ l^{-1}$	0.1	76	2	0.3	80	5	0.5	25	5	0.5	51	7
Zn	$\mu g\ l^{-1}$	0.1	130	7	0.5	370	22	0.5	85	19	0.5	120	16
Al	$\mu g\ l^{-1}$	<1	5400	125	<1	6100	198	5	590	131	<1	6500	843
NO_3–N	$\mu g\ l^{-1}$	<1	1300	114	<1	7600	263	<1	2400	713	3	410	93
NH_4–N	$\mu g\ l^{-1}$	<1	920	18	<2	960	38	<1	970	217	<1	250	21
PO_4–P	$\mu g\ l^{-1}$	<1	94	9	<1	370	23	<2	360	33	<1	35	9

eastern and southwestern Finland the fluoride contents of groundwater are exceptionally high as compared with the values for the whole country (Lahermo and Rainio 1972). In the basic rock type areas of northern Finland the fluorine content is clearly lower than in the granite and mica areas of southern Finland. The acidic rock types, rich in silicic acid, have a great influence on the fluoride content of the groundwater, especially in granite and rapakivi areas (Table 30).

The fluoride content of groundwater varies within areas containing different rock types as well as within areas having only one major rock type. This is partly due to the glacial transport of sediments, creating differences in mineral composition between bedrock and overburden.

The fluoride content of groundwater correlates also on the hardness of the water, its content of sodium bicarbonate, conductivity and pH (Fig. 28, Tables 31 and 32). A high pH-value is normally associated with a high content of fluoride (Jacks 1973 a).

The circulation of fluoride between soil, sea and atmosphere can be compared to that of chloride. Thus fluoride deposition is also highest near to marine areas. In Finland the F/Cl-ratio of snow fall varies generally from 0.2 to 0.4.

The temporal fluctuations of the concentration of fluoride in groundwater were compared with fluctuations of groundwater stage in two different bedrock areas, at Tullinkangas (4) and Valkeala (14).

Tullinkangas is a basic bedrock area, where the fluoride level is very low, on average 40 μg l^{-1}, whereas at Valkeala, in the rapakivi-granite area,

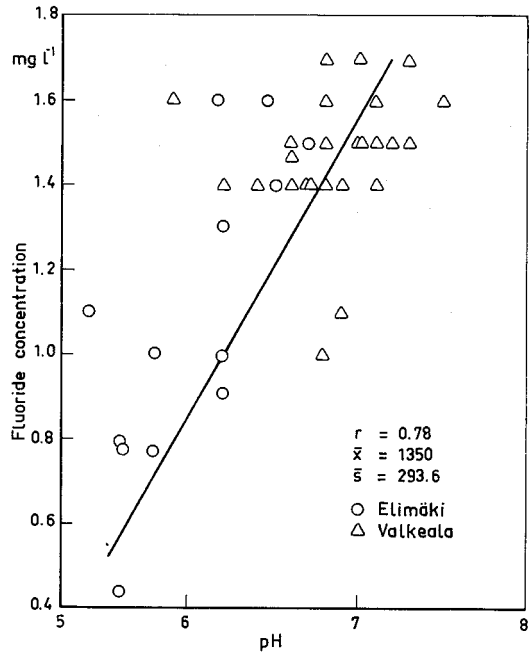

Fig. 28. The correlation between fluoride concentrations and pH values in groundwater in the Elimäki and Valkeala rapakivi-granite area of southern Finland.

Table 30. The minimum, maximum and mean values of the fluoride content (μg l^{-1}) of the groundwater in different rock types at the groundwater stations. (n_1 = number of examination points, n_2 = number of analyses) (Soveri and Soveri 1981).

Rock type	n_1	n_2	Fluoride μg l^{-1}		
			min	max	mean
Rapakivi-granite	3	47	300	2400	1500
Veined and mica gneiss	7	90	40	370	125
Granite	12	173	40	310	120
Diorite	11	129	50	140	90
Mica schist	6	45	50	130	80
Granite-gneiss	9	146	40	120	70
Migmatite	2	30	40	50	45
Cabbro, amphibolite and hornblende gneiss	3	55	30	80	45
Arkose sandstone	1	7	30		30
The whole country	54	732	30	2400	150

Table 31. Correlation coefficients between fluoride and some other parameters of groundwater in the rapakivi-granite area.

	F	Ca	PO_4–P	K	Mg	pH
F	1.00					
Ca	0.10	1.00				
PO_4–P	0.60	0.14	1.00			
K	0.09	0.05	0.06	1.00		
Mg	0.43	0.28	0.50	0.22	1.00	
pH	0.78	0.02	0.40	0.11	0.64	1.00

Table 32. Correlation coefficients between fluoride and some other parameters of groundwater in the whole country.

	F	Ca	PO_4	K	Mg	pH	γ_{25}
F	1.00						
Ca	0.08	1.00					
PO_4–P	0.03	0.25	1.00				
K	0.09	0.41	0.26	1.00			
Mg	0.10	0.43	0.17	0.61	1.00		
pH	0.16	0.34	0.08	0.25	0.21	1.00	
γ_{25}	0.17	0.69	0.32	0.56	0.62	0.21	1.00

the fluoride content may be as high as 1500 μg l^{-1}.

In Tullinkangas the fluctuations of fluoride concentration are clearly connected with groundwater recharge. An increase in the groundwater level is accompanied by an increase in the fluoride content (Fig. 29). This is due to the fluoride content of meltwater and rainwater and is not connected with leaching from the bedrock.

In the Valkeala rapakivi-granite area the fluoride concentrations of the groundwater changed in relation to the groundwater recharge in a manner quite the opposite to that at Tullinkangas. At Valkeala, a rise in the groundwater level caused a decrease in the fluoride concentration (Fig. 29). This was due to dilution of the fluoride concentration of the groundwater by meltwater. Further, decrease of the groundwater level resulted in retention of water, allowing more time for leaching and thus leading to an increase in the fluoride concentration.

The relationships between substance concentrations in groundwater were also examined in different rock types with the aid of a correlation matrix (Tables 33—36).

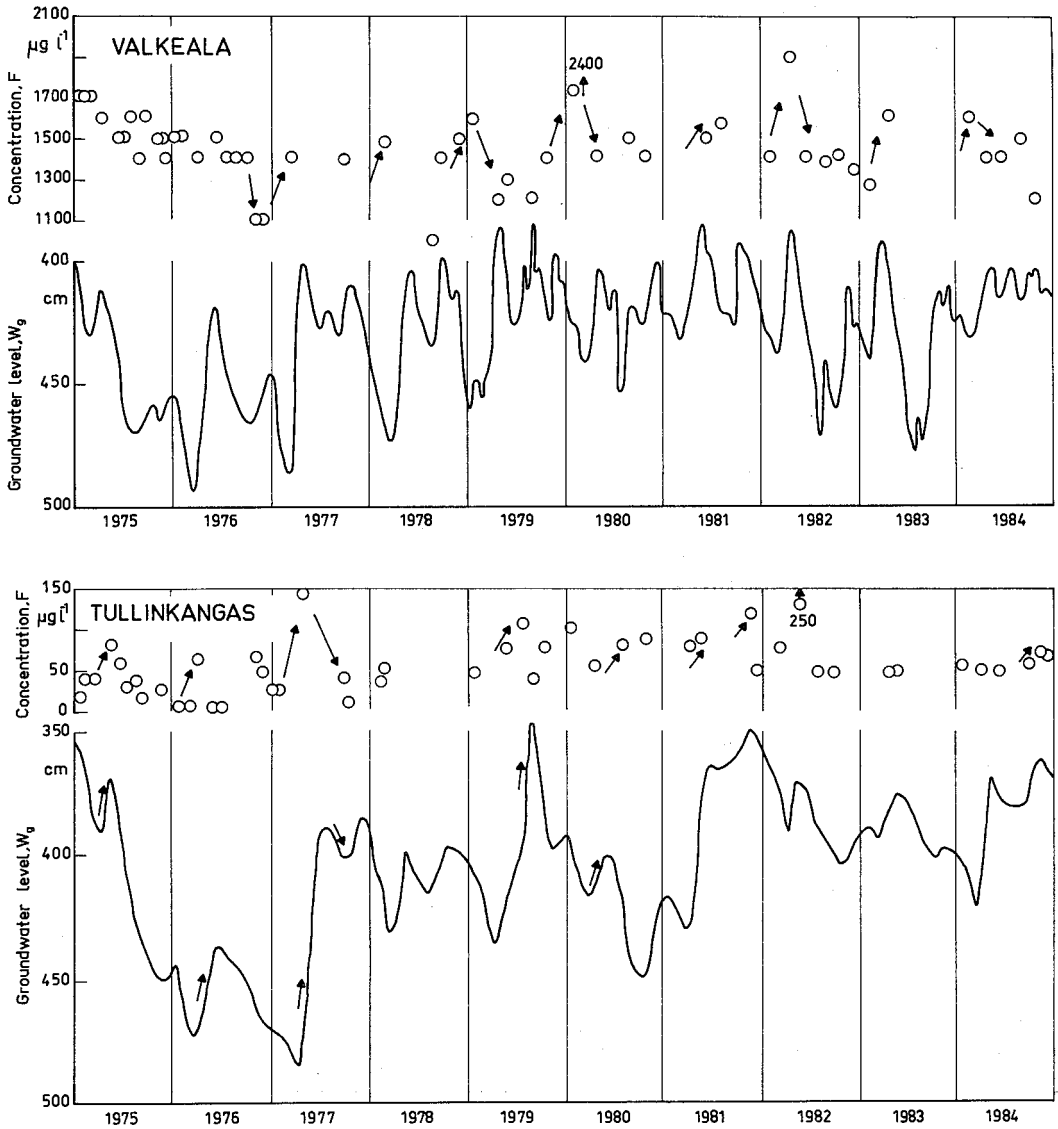

Fig. 29. Fluoride concentrations of groundwater in relation to fluctuations of the groundwater level in the basic bedrock area of Tullinkangas (lower figure) and in the rapakivi-granite area of Valkeala (upper figure).

Table 33. Correlations between the pH, electrical conductivity and substance concentrations of groundwater in areas with acidic bedrock.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.84***	1.00																
pH	0.43***	0.59***	1.00															
NO_3–N	0.34***	0.12***	0.03	1.00														
NH_4–N	0.02	0.04	0.16***	0.10**	1.00													
PO_4–P	0.12***	0.13***	0.12***	0.06*	0.27***	1.00												
Cl	0.52***	0.29***	0.19***	0.57***	0.04	0.00	1.00											
Mn	0.03	0.04	0.17***	0.07*	0.90***	0.35***	0.05°	1.00										
Al	0.14**	0.16***	0.15***	0.05	0.24***	0.30***	0.03	0.33***	1.00									
F	0.31***	0.26***	0.12**	0.03	0.28***	0.01	0.14**	0.30***	0.07	1.00								
K	0.43***	0.29***	0.00	0.46***	0.29***	0.09**	0.43***	0.28***	0.16***	0.02	1.00							
Ca	0.82***	0.80***	0.63***	0.18***	0.01	0.14***	0.34***	0.02	0.12**	0.33***	0.22***	1.00						
Cu	0.13***	0.18***	0.25***	0.04	0.13***	0.08**	0.16***	0.08*	0.33***	0.15**	0.18***	0.16***	1.00					
Pb	0.15***	0.18***	0.17***	0.07*	0.18***	0.15***	0.10**	0.09**	0.55***	0.15***	0.23***	0.13***	0.48***	1.00				
Mg	0.74***	0.67***	0.11***	0.29***	0.10**	0.08**	0.44***	0.05	0.04	0.15***	0.46***	0.49***	0.07*	0.05	1.00			
Na	0.77***	0.68***	0.18***	0.30***	0.06*	0.05	0.55***	0.09**	0.09	0.34***	0.42***	0.55***	0.19***	0.16***	0.73***	1.00		
Zn	0.11***	0.19***	0.26***	0.09**	0.19***	0.06*	0.11***	0.14***	0.45***	0.12**	0.24***	0.13***	0.54***	0.67***	0.05	0.14***	1.00	
SO_4	0.57***	0.33***	0.03	0.10**	0.12***	0.04	0.17***	0.06*	0.08°	0.37***	0.07*	0.47***	0.14***	0.14***	0.41***	0.51***	0.04	1.00

Table 34. Correlations between the pH, electrical conductivity and substance concentrations of groundwater in areas with schistose bedrock.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.85***	1.00																
pH	0.56***	0.57***	1.00															
NO_3–N	0.28***	0.07	0.04	1.00														
NH_4–N	0.46***	0.41***	0.15***	0.08*	1.00													
PO_4–P	0.42***	0.27***	0.08	0.27***	0.49***	1.00												
Cl	0.56***	0.27***	0.12**	0.68***	0.30***	0.47***	1.00											
Mn	0.58***	0.39***	0.31***	0.08*	0.53***	0.43***	0.35***	1.00										
Al	0.05	0.01	0.16**	0.05	0.28***	0.22***	0.14*	0.22***	1.00									
F	0.42***	0.20***	0.17**	0.03	0.25***	0.39***	0.34***	0.53***	0.07	1.00								
K	0.55***	0.31***	0.17***	0.81***	0.20***	0.63***	0.76***	0.24***	0.04	0.22***	1.00							
Ca	0.91***	0.85***	0.57***	0.09*	0.43***	0.33***	0.36***	0.62***	0.00	0.44***	0.36***	1.00						
Cu	0.01	0.03	0.21***	0.03	0.18***	0.17***	0.05	0.02	0.12*	0.05	0.05	0.07	1.00					
Pb	0.20***	0.12**	0.01	0.09*	0.23***	0.20***	0.18***	0.44***	0.12*	0.16*	0.12**	0.21***	0.41***	1.00				
Mg	0.74***	0.84***	0.34***	0.07	0.39***	0.34***	0.29***	0.40***	0.08	0.18**	0.33***	0.76***	0.00	0.04	1.00			
Na	0.67***	0.49***	0.36***	0.41***	0.34***	0.54***	0.64***	0.44***	0.11*	0.34***	0.64***	0.49***	0.17***	0.39***	0.34***	1.00		
Zn	0.21***	0.05	0.00	0.76***	0.03	0.35***	0.56***	0.01	0.01	0.03	0.72***	0.06	0.14***	0.09*	0.06	0.40***	1.00	
SO_4	0.64***	0.35***	0.38***	0.12**	0.40***	0.40***	0.50***	0.78***	0.07	0.70***	0.36***	0.66***	0.02	0.36***	0.23***	0.51***	0.11*	1.00

Table 35. Correlations between the pH, electrical conductivity and substance concentrations of groundwater in areas with basic bedrock types.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.40***	1.00																
pH	0.32**	0.41***	1.00															
NO_3–N	0.59***	0.16	0.50***	1.00														
NH_4–N	0.79***	0.20	0.56***	0.68***	1.00													
PO_4–P	0.61***	0.65***	0.02	0.44***	0.50***	1.00												
Cl	0.59***	0.29**	0.29***	0.44***	0.29**	0.46***	1.00											
Mn	0.89***	0.48***	0.73***	0.65***	0.83***	0.40***	0.40***	1.00										
Al	0.82***	0.32*	0.79***	0.66***	0.83***	0.53***	0.48**	0.78***	1.00									
F	0.67***	0.14	0.77***	0.75***	0.73***	0.41**	0.59***	0.83***	0.85***	1.00								
K	0.67***	0.38***	0.02	0.19	0.45***	0.45***	0.49***	0.34**	0.34*	0.31*	1.00							
Ca	0.90***	0.60***	0.18	0.55***	0.72***	0.65***	0.70***	0.74***	0.59***	0.54***	0.62***	1.00						
Cu	0.55***	0.08	0.40***	0.32**	0.29*	0.19	0.17	0.50***	0.40*	0.30*	0.33**	0.26*	1.00					
Pb	0.68***	0.19	0.34**	0.42***	0.54***	0.57***	0.39***	0.60***	0.60***	0.42**	0.47***	0.49***	0.50***	1.00				
Mg	0.93***	0.39***	0.36***	0.67***	0.84***	0.64***	0.71***	0.86***	0.72***	0.77***	0.68***	0.88***	0.53***	0.67***	1.00			
Na	0.87***	0.37***	0.16	0.52***	0.63***	0.65***	0.67***	0.60***	0.49**	0.57***	0.77***	0.77***	0.54***	0.64***	0.86***	1.00		
Zn	0.65***	0.15	0.76***	0.51***	0.65***	0.53***	0.42***	0.67***	0.58***	0.69***	0.04	0.62***	0.30*	0.52***	0.70***	0.41***	1.00	
SO_4	0.91***	0.05	0.64***	0.69***	0.86***	0.42***	0.43***	0.94***	0.81***	0.86***	0.44***	0.73***	0.53***	0.55***	0.87***	0.67***	0.70***	1.00

Table 36. Correlations between the pH, electrical conductivity and substance concentrations of groundwater in areas with miscellaneous bedrock types.

	γ_{25}	Alk	pH	NO_3–N	NO_4–N	PO_4–P	Cl	Mn	Al	F	K	Ca	Cu	Pb	Mg	Na	Zn	SO_4
γ_{25}	1.00																	
Alk	0.87***	1.00																
pH	0.45***	0.27***	1.00															
NO_3–N	0.24**	0.06	0.23**	1.00														
NH_4–N	0.39***	0.33***	0.37***	0.03	1.00													
PO_4–P	0.41***	0.27***	0.53***	0.35***	0.23**	1.00												
Cl	0.14	0.26***	0.52***	0.20**	0.11	0.38***	1.00											
Mn	0.79***	0.64***	0.60***	0.17*	0.47***	0.62***	0.22**	1.00										
Al	0.44***	0.12	0.57***	0.43***	0.25*	0.82***	0.28**	0.72***	1.00									
F	0.20	0.00	0.32**	0.18	0.11	0.06	0.42***	0.23*	0.21	1.00								
K	0.11	0.01	0.25**	0.36***	0.00	0.54***	0.21**	0.30***	0.67***	0.21*	1.00							
Ca	0.21**	0.19**	0.38***	0.05	0.09	0.19*	0.52***	0.06	0.17	0.26**	0.11	1.00						
Cu	0.42***	0.36***	0.25**	0.16	0.17*	0.31***	0.17*	0.42***	0.32**	0.27*	0.16	0.03	1.00					
Pb	0.60***	0.54***	0.36***	0.14	0.49***	0.46***	0.20*	0.64***	0.56***	0.14	0.22**	0.02	0.43***	1.00				
Mg	0.88***	0.79***	0.64***	0.32***	0.40***	0.55***	0.45***	0.77***	0.57***	0.08	0.21**	0.01	0.46***	0.60***	1.00			
Na	0.94***	0.84***	0.52***	0.21**	0.47***	0.51***	0.26***	0.88***	0.59***	0.24*	0.15	0.05	0.48***	0.67***	0.89***	1.00		
Zn	0.56***	0.46***	0.36***	0.23**	0.16*	0.35***	0.22**	0.56***	0.37**	0.31**	0.19*	0.03	0.78***	0.45***	0.59***	0.58***	1.00	
SO_4	0.51***	0.29***	0.79***	0.42***	0.30***	0.56***	0.58***	0.62***	0.68***	0.14	0.34***	0.31***	0.32***	0.37	0.68***	0.58***	0.39***	1.00

The effect of solubility on groundwater quality is smallest in acidic pre-cambrian orogenic rocks. This was also revealed in the correlation matrices, in which the weakest interdependence of substance concentrations occurred in the case of such acidic rock types.

The most obvious effect of mineral solubility on groundwater materials was observed in areas in which basic rock types predominated. In these areas the correlations between almost all of the elements were statistically significant. Lahermo (1970) also reported that basic rock types have the greatest effect on the total ionic concentration of groundwater.

Variations in the amount and quality of groundwater are not always cyclic or coordinated. They are mainly affected by the following factors:

— amount and temporal distribution of precipitation
— uptake of nutrients by vegetation
— leaching
— enrichment of materials in surface soil layers by evapotranspiration
— soil moisture deficit of the unsaturated zone and the oxidation-reduction conditions prevailing in the soil
— variations in the height of the groundwater level
— stratification, mixing and discharge of the groundwater aquifer

The stratification, mixing and discharge of the groundwater have the greatest effect on the cyclic variation of groundwater quality. For example, a water sample taken from a spring may not be representative of the newly-formed groundwater but may originate from older water at the bottom of the aquifer or be mixed with new meltwater. For this reason trends in groundwater quality are often not coincident with changes in the amount of groundwater. Rather, there is always a time lag between changes in the amount and the quality of groundwater. This differential varies between aquifers and between years according to the prevailing climatic conditions.

5.3 Chemical input and output in the saturated zone

Changes in soil water composition after the percolation resulting from the spring thaw were examined at some groundwater stations by input-output analysis (Input = Output ± Change in the saturated zone).

Changes in pH, electrical conductivity and certain substance concentrations in groundwater with respect to the corresponding values for infiltration water are presented in Table 37 for areas with sorted and unsorted soil types. The change is positive if the concentration is greater in groundwater than in infiltration water and negative in the opposite case.

Changes in pH, electrical conductivity and sulfate were clearly negative in the groundwater. Although the concentration of sulfate decreased, the acidity of the water increased. This was most

Table 37. The input-output concentration balance of infiltration water and groundwater at certain groundwater stations.

Groundwater station	GW—IW											
	pH	γ_{25} mS m^{-1}	SO_4 mg l^{-1}	Cl mg l^{-1}	Na mg l^{-1}	K mg l^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	Cu µg l^{-1}	Mn µg l^{-1}	PO_4–P µg l^{-1}	Pb µg l^{-1}
Sorted soils												
Jämijärvi (1978)	−0.5	−4.3	−2.7	0.1	0.7	−0.3	−0.5	0.0	—	−5	4.0	0.5—2
Pistohiekka (1981)	−0.5	−2.8	−4.3	0.8	—	—	—	—	2	—	2.0	0.5—1
Naakkima (1981)	−0.1	3.4	−5.5	0.7	—	—	—	—	5	—	12.0	0.5—1
Kangaslahti (1980)	−1.2	−1.5	—	−0.2	—	0.5	−0.3	0.1	0.5—50	1	2.0	−1
Kuuksenvaara (1978)	−1.5	−6.8	−17.3	0.2	0.3	0.2	−4.7	0.1	40	−44	3.0	0
Jaamankangas (1978)	−1.2	−8.9	−19.0	−0.3	−0.2	0.1	−8.9	−1.2	4	−10	5.0	−4
Juutilankangas (1980)	−0.9	−5.2	−24.9	6.7	1.7	1.2	−8.0	0.7	0.5—15	4	6.0	0.5—3
Ruukki (1980)	−0.9	−1.9	−2.2	0.9	0.4	−0.4	0.1	−0.2	0.5—3	—	0.0	0.5—5
Nellim (1981)	−0.5	−4.6	−4.7	0.4	−0.8	0.7	2.0	0.4	−3	13	−3.0	0.5—1
$\bar{x}$	−0.8	−3.6	−10.1	+0.1	+0.4	+0.3	−3.5	0	~	~	+3.0	~
Unsorted soils												
Heinävesi (1981)	0.1	5.2	−2.7	−0.5	−0.5	−1.0	14.4	1.5	2	−12	17.0	0.5—1
Akonjoki (1980)	−0.3	−4.2	−2.3	0.4	0.2	−1.0	—	1.4	−13	—	15.0	30
Vehkoo (1981)	−0.3	0.5	—	1.9	1.3	0.2	3.4	0.8	0.5—6	−7	6.0	0.5—1
Kolmisoppi (1979)	−0.2	−7.8	−14.6	−0.3	0.0	−1.2	−16.5	−0.5	1	−101	2.0	−12
$\bar{x}$	−0.2	−1.6	− 6.5	+0.4	+0.3	−0.8	+0.4	+0.8	~	~	+10.0	~

obvious in aquifers in which sorted soil types were predominant.

The concentrations of alkali and earthalkali metals increased slightly in the groundwater after infiltration, reflecting the low solubility of these metals in the conditions of the saturated zone. The neutralizing effect of basic cations on groundwater acidity was only slight in shallow aquifers. Only when the retention time of the groundwater in the soil is sufficiently long do the basic cations begin to neutralize groundwater. In deep aquifers the pH of groundwater is always higher than in shallow aquifers, regardless of the type of bedrock (Knutsson et al. 1981).

6. GROUNDWATER RECHARGE AND ITS TEMPORAL AND SPATIAL VARIATION IN SHALLOW AQUIFERS

In temperate and humid environments, where annual precipitation generally exceeds the annual potential evaporation, groundwater is recharged mainly by rainfall. Groundwater flow in these areas will tend to be towards lakes and rivers, where it becomes the base flow component of the surface water.

Where groundwater is recharged mainly from rainfall the changes in groundwater level depend on the characteristics and state of the aquifer and overlying soil. Important factors are the degree of saturation, effective porosity and permeability of the soil and the distance that infiltrating water has to travel to reach the groundwater table. These factors all contribute to the delay in the reaction of the groundwater table to rainfall. In Finland and in the other Nordic Countries this delay is usually short, as the soil layer is generally rather thin and predominantly Quaternary. This causes the groundwater table to follow closely the annual rhythm of seasonal changes. In most geological formations of Finland groundwater recharge is strongly seasonal, taking place mainly in the spring and autumn months.

6.1 Groundwater fluctuations in different soils

The hydrostatic pressure at the surface of the groundwater corresponds to the prevailing atmospheric pressure. The groundwater surface softly follows the topography of the soil surface. The relationship between the soil surface and, that of the groundwater varies in different soil types. This interdependence is most obvious in clay, silt and moraine deposits above the bedrock. The deviation of groundwater surface from the indications provided by soil topography is greatest in permeable deposits like eskers and similar glaciofluvial deposits (Gustafsson 1968, Soveri 1973).

Groundwater basin tends to fluctuate continuously in response to external factors in both confined and unconfined aquifers. Corresponding fluctuations occur in the groundwater table, where variations in level may be either relatively rapid, as in the case of seasonal variation, or long-term with a duration of several years. The short-term variations may be caused by changes in atmospheric pressure, earth tremors, precipitation or seepage of surface water. In addition human interference, such as the regulation of watercourses, drainage, and earthworks may cause rapid, either short-term or permanent changes in level.

This section is concerned with variations in groundwater level caused by seasonal changes in the hydrological cycle and with long-term changes caused by climatological variations.

Changes in groundwater storage occur because of differences between inflow and outflow rates to and from groundwater. These differences vary in space and time, particularly from one climatological zone to another, due to different precipitation and evaporation patterns. In some areas groundwater recharge may be derived predominantly from rainfall directly and in other areas from the infiltration of surface water. Groundwater level fluctuations in a given locality tend to occur in a regular manner so that they may be used as an index of the regime characteristics.

6.11 Seasonal variation of groundwater level

As the availability of percolating water is largely controlled by the degree of evapotranspiration, seasonal patterns of change exist. Nordberg and Persson (1976) found in Sweden that seasonal patterns can be classified into four main regime types corresponding to climatological conditions. The patterns are valid for all types of shallow aquifers in till and water-laid sediments and in crystalline bedrock. Deep-lying unconfined aquifers in large glaciofluvial deposits and in sedimentary bedrock beneath thick, loose sediments react with a time lag, giving a displaced pattern. In this study

time lag means the time difference between snow melt and groundwater recharge.

The diagrams in Fig. 30 show the mean seasonal groundwater variation patterns in Finland. The groundwater curves are based on monthly mean levels from 45 representative groundwater stations from the last 5—9 years. The tentative zonation is based on these observation stations.

The time span of the diagrams in Fig. 30 is one calender year and the height of the curves corresponds to the maximum amplitude of the monthly groundwater means. The diagrams represent the annual variation of the upper and lower limits of the groundwater surface. The height of the diagram is same in all cases.

On the basis of these long-term observations it is possible to discriminate from the seasonal groundwater fluctuations four different regions. The annual variation has a different characteristic pattern in each region reflecting the prevailing climatological conditions.

In the northern Finland and Kainuu (Region 1), the recharge of groundwater reserves occurs mainly as a result of melting of snow in April, May and June. Despite summer rainfall the groundwater storage generally decreases during the summer months as a result of evapotranspiration and depletion. Even the autumn rains do not fill the groundwater reserves, but the reserves begin to empty immediately after their recharge and reach their minimum level just before the melting of snow in spring. In Region I the recharge and discharge of the groundwater reserve can clearly be seen as a two-stage process.

The pattern of type II shows a more clear influence of the autumn. Also in region II a major recharge in connection with snowmelt is noticed but also a minor recharge in the autumn before the precipitation turns into snow. This pattern is mainly found in central and southern Finland. The variation of the groundwater surface has four stages, with two minimum and two maximum values of the groundwater reserve. The lowest groundwater level occurs during late winter just before the start of snowmelt.

A pattern of type III indicates a secondary decrease in groundwater level in the winter and is most frequently observed in south-western Finland and in coastal regions in the south and west of the country. Also in this zone the variation of the groundwater level has four stages, but the annual minimum always occurs after the summer season and a secondary minimum in late winter. Recharge of groundwater reserves during autumn rainfall is most significant in this regime, in which the groundwater level usually reaches its annual maximum in late autumn before the freezing of the soil.

Pattern IV is unusual in Finnish conditions and occurs only in some parts of the Ahvenanmaa archipelago. This regime is, however, quite common in southern Sweden, Denmark and central Europe (Nordberg and Soveri 1978). Formation of groundwater takes place in this region in both spring and autumn but also during the winter, when evaporation is minimal and the effect of precipitation on groundwater production is great. The level of groundwater is always at its highest in early summer after the thaw and plentiful spring precipitation. The groundwater level falls rapidly from its maximum to its minimum value during the summer months and is lowest in late summer or early autumn, i.e. in August-September. The temporal curve of groundwater stage in areas with this regime has two phases.

The formation of groundwater in Finland varies considerably as a result of climatic factors. The temporal curves of groundwater height in regimes I and IV behave in opposite ways, so that the time differential between the achievement of maximum groundwater height in the southern and northern parts of Finland is almost six months. The geohydrological regime division presented above also follows regional divisions made on the basis of other hydrological parameters (e.g. Hyvärinen 1977, Solantie 1978, Kuusisto 1984).

The established patterns of mean seasonal variations can be used as rough prediction models for groundwater levels. For many areas the peak and minimum situations can be predicted with regard to both time and relative level. Knowledge of the nature of the time lag in different soil types and damping of long-term variations can both be utilized in prediction work.

6.12 Annual variation of groundwater level

The long-term natural behaviour of aquifers is controlled by the long-term ratio of recharge to discharge. Whereas the discharge of an aquifer is highly dependent of hydraulic properties that do not change with time, the recharge is controlled by such changing variables as precipitation and evapotranspiration.

The succession of annual mean groundwater levels provides a picture of the relationships between discharge and recharge that can be attributed to climatological conditions. To minimize the local effects of various hydraulic properties within and around different aquifers, a method developed by Konoplyantsev (1970) is used, in

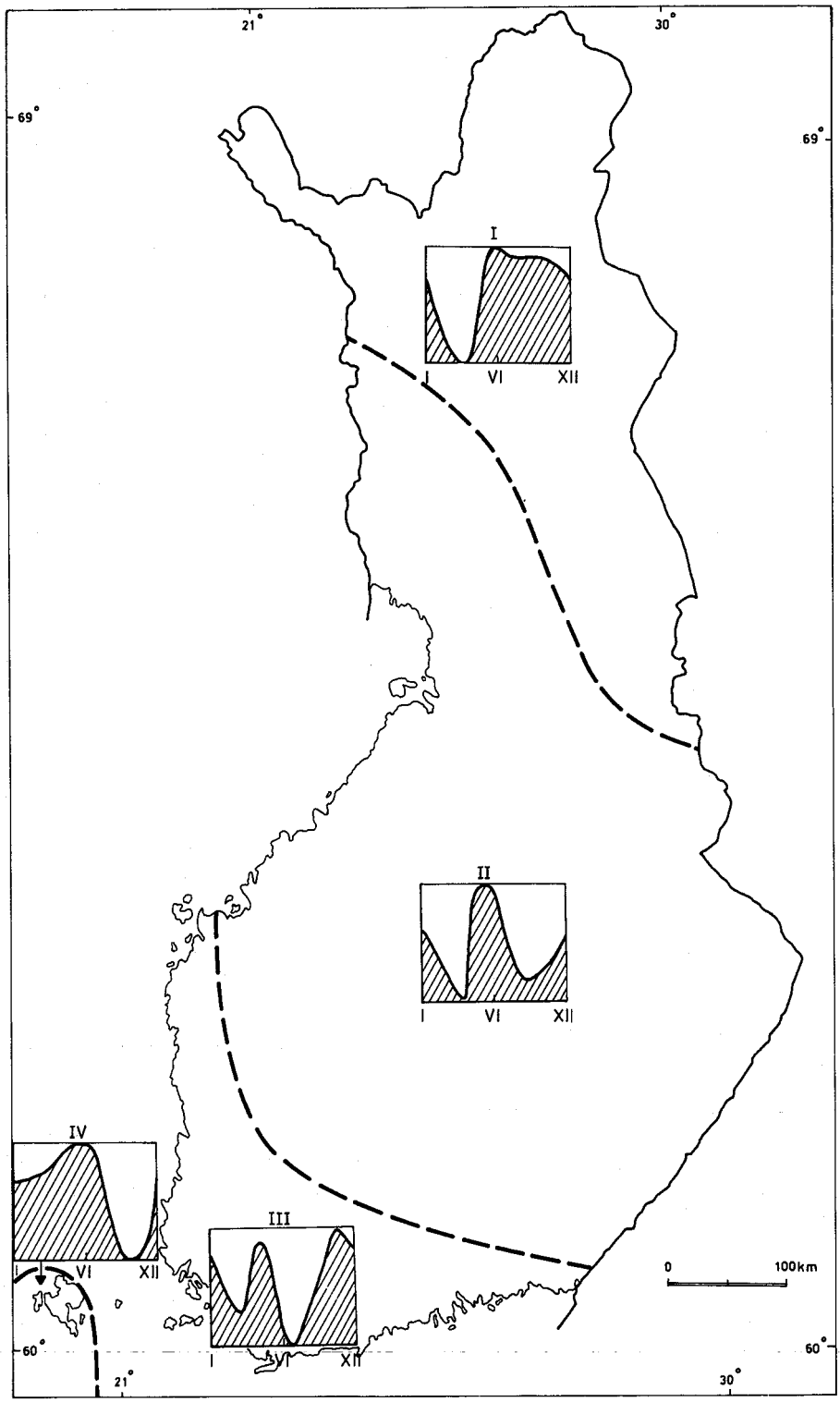

Fig. 30. The four different patterns and corresponding regions of groundwater fluctuation.

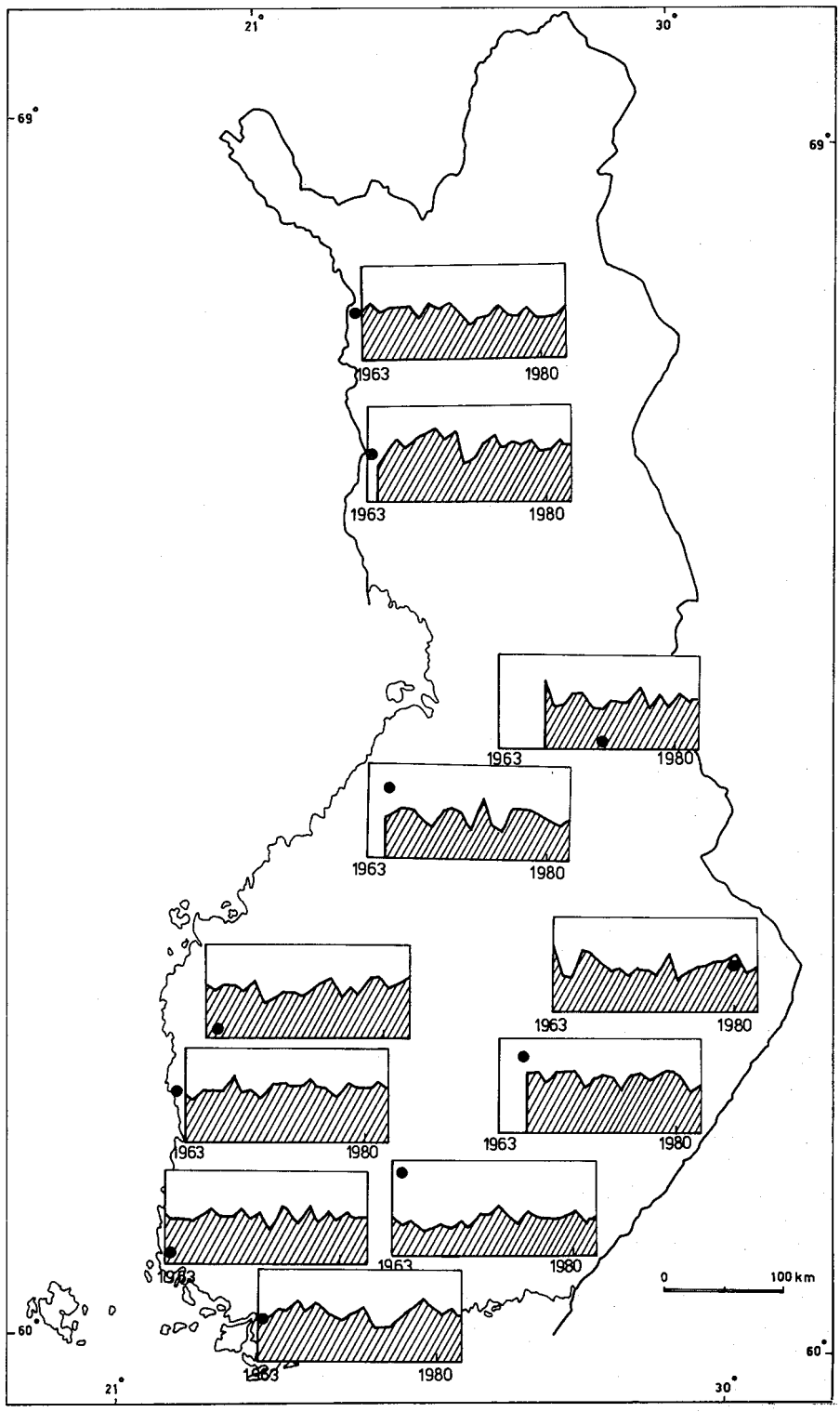

Fig. 31. Annual variations in groundwater level at selected representative stations. The height of the diagrams corresponds to the observed maximum amplitude for the observation period 1963–1983.

which the annual mean level is related to the observed maximum amplitude for the whole period of observation, i.e.

$$\lambda = \frac{MW_g - NW_g}{HW_g - NW_g}, \quad (55)$$

where

λ = coefficient of relative groundwater level
MW_g = annual mean groundwater level
HW_g = maximum groundwater level
NW_g = minimum groundwater level

The annual mean groundwater level is determined by both climatological and geological factors. As was shown in Fig. 31, the seasonal variations differ considerably from the southern to the northern part of Finland. The main discriminent is the melting of snow, which occurs 1—3 months later in the north than in the south. Winter accumulation of snow and the mode of melting therefore play a major role in determining the mean groundwater level. There is a generally increasing time lag between precipitation and groundwater recharge when proceeding northwards.

The hydrogeological properties of the aquifer and the unsaturated zone control the response of the groundwater to rainfall and snowmelt. A deeplying unconfined aquifer may react with a delay of several months. The materials presented here is derived from groundwater stations in aquifers with a relatively small and uniform time lag (1—2 months).

The diagrams in Fig. 31 represent the years 1962—1983 or shorter periods from selected representative observation stations of the National Board of Public Roads and Waterways (Johansson and Soveri 1965).

The different time lags influence the individual annual groundwater mean levels, which must be considered when making comparisons between aquifers.

Another difficulty is introduced by the nonuniform length of the period of observation at different observation stations. Because of this, the curves are directly comparable only between stations with identical observation periods (Nordberg and Soveri 1978).

From the diagrams in Fig. 31, a clear although slight trend towards increasing groundwater levels can be distinguished in south and southwestern Finland. This trend coincides with a period of unusually high precipitation. The effects have been recorded in aquifers of many types; small and large, deep and shallow, confined and unconfined. Due to varying local conditions, however, individual local trends in the opposite direction have also been observed within the area of increasing groundwater levels.

In eastern Finland no clear, regional trends are found. However, several stations in northern Finland show decreasing groundwater levels during the 1970s and 1980s.

The absolute change of groundwater level is qualified by the effective porosity and permeability of the soil and may vary during a year from centimeters to several meters. This aspect is not considered in this report.

Significant periodicities within the long-term variations have not been found, one reason being the rather short period of observation. Zalzberg (1977) reported periodicities of 4—5, 8—11, 16—17 and 25—27 years for groundwater in western Soviet Union.

In Czechoslovakia Kříž (1972) found that the periodicity of the fluctuations of groundwater storage between 1901 and 1970 was not most frequently three to six years. Only in exceptional cases was the cycle longer.

In many cases the commonest periodicity of groundwater level in Finland is also 3—4 years, at Pieksämäki and Oulainen (Fig. 32). However, a 21 year observation period is insufficient for the demonstration of a regularly repeating periodicity cycle. Climatic variations are not in themselves sufficient to explain all the changes in groundwater level.

6.13 Duration analysis of groundwater level

The duration curve is a cumulative frequency curve showing the time during which a certain water level value is equalled or exceeded. Usually the time is expressed in days per year or as a percentage of the whole time period under observation.

The stability of the groundwater level in different soil types was examined in different groundwater regimes in sorted and unsorted soils. For this stability analysis the regional means of annual variation in water level were calculated for each of the groundwater regions over the period 1976—1983.

The duration curves presented in Fig. 32 were drawn using a percentage scale for duration and a linear scale for the groundwater stage. The water stage scale is the same for all the hydrograph curves, and the gauge data can therefore easily by compared (Reuna 1979).

The duration curve describes the mean annual variation of groundwater height. At the same scale the curve is shallow if variations were slight and

steep in the case of extensive variation.

Although the groundwater level variations in different regimes are either two or four phased, the duration curves do not differ markedly in different parts of the country.

The extreme amplitudes of groundwater level are found in moraine soil. The temporal percentage of low groundwater level is also greater in moraine soil than the percentage of high level (e.g. Regime II).

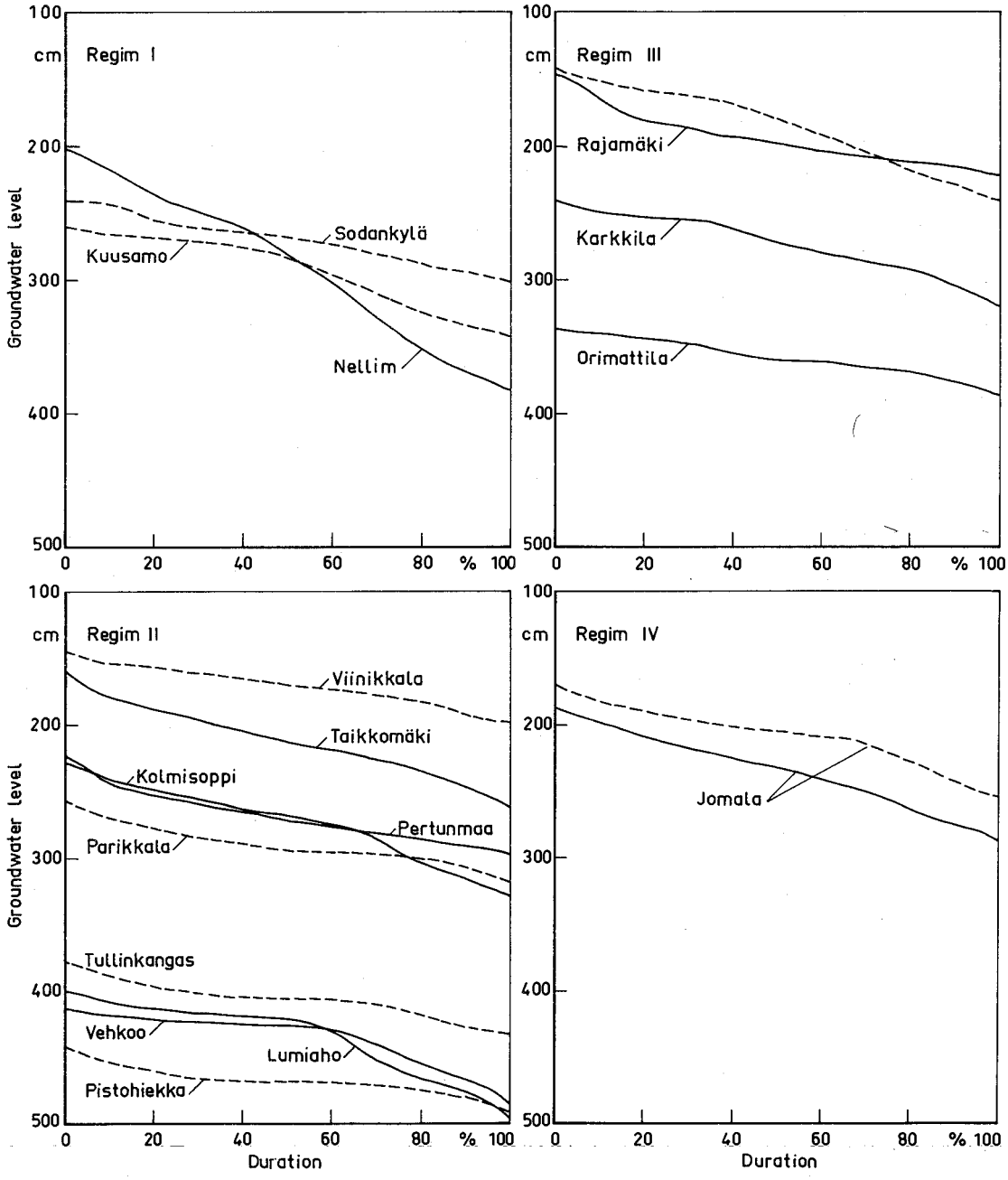

Fig. 32. The mean duration curves of groundwater level for the observation period 1976—1983 in different groundwater regimes in unsorted (broken lines) and sorted (full lines) soils.

6.2 Groundwater recharge from meltwater

One of the most important factors in the determination of groundwater resources is the estimation of natural recharge to aquifers. Groundwater recharge occurs when the residual precipitation (precipitation less evaporation) has infiltrated to the groundwater table. This may occur from several hours to several months after the rainfall or snowmelt event.

Gottschalk and Nordberg (1977) have presented a mathematical model for the response of groundwater level to infiltration. They showed that large, glaciofluvial eskers with thick unsaturated zones have a small and slow response, whereas till has a large and rapid response.

The recharge due to snowmelt is of greatest significance in northern and central parts of Finland, where the main recharge event occurs as a result of the snowmelt in spring. The time lag between snowmelt and the response of groundwater level is therefore most clear-cut in these parts of the country.

The rise in groundwater level due to melting water is proportional to the effective porosity of the soil and the ratio of the volume of interconnected pore-space available for fluid transmission to the bulk volume of the soil or rock (Johansson 1984 ed.)

The effective porosity varies between till and glaciofluvial soil on average from about 5 to 30 % (e.g. Richter and Lillich 1975, Lemmelä 1976).

Groundwater levels, the duration and water equivalent of the snow cover, the conditions of soil freezing and air temperature are the parameters which are recorded for the evaluation of groundwater recharge from snowmelt. These data are usually easy to record and the method is therefore suitable for fluctuation analysis.

In the following, the immediate effect of meltwater on groundwater formation in different soil types is examined on the basis of changes in water level. The examples were chosen from different groundwater formation regimes during 1984, when record amounts of snow fell in some parts of the country (Monthly hydrological report for 1984).

The following terms, used in sections 6.21 and 6.22, are illustrated in Fig. 33.

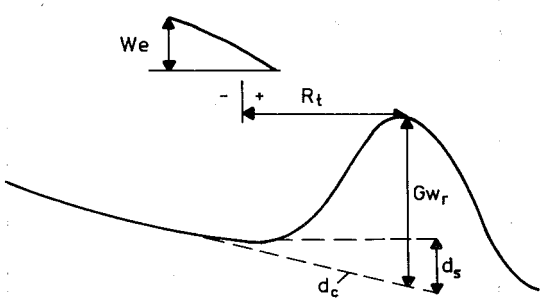

Fig. 33. The effect of snowmelt on the response of groundwater level. R_t = response time between the maximum groundwater level and the beginning of positive daily air temperatures; d_c = approximate groundwater depletion curve; d_s = depletion speed of groundwater level; GW_r corrected groundwater rise; We_{max} = maximum water equivalent of snow.

6.21 Recharge in till aquifers

The effect of meltwater on the level of groundwater was investigated in moraine aquifers in spring 1984 at the groundwater stations of Kullisuo (Regime I), Mutkala (Regime II) and Elimäki (Regime III). The grain-size distribution curves describing the soil are presented in Fig. 34 and the geohydrological parameters used in hydrograph analysis is presented in Table 38.

The soil types at Kullisuo and Mutkala were rather similar, but the moraine at Elimäki was considerably finer. Estimated on the basis of the sand percentages of the soil types, the effective porosities and water retention capacities of the

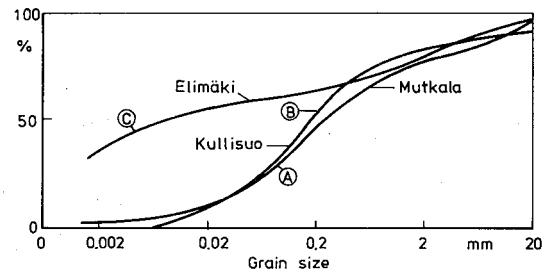

Fig. 34. Grain size distribution of representative till soils at the groundwater stations at Mutkala (A), Kullisuo (B) and Elimäki (C).

Table 38. Some geohydrological parameters of till soils used in groundwater hydrograph analysis (see list of symbols).

Groundwater Station	Regime	Sand %	W_g cm	We_{max} mm	d_s cm month^{-1}	R_t d	GW_r cm
Kullisuo	I	37	−220	210	13	33	130
Mutkala	II	31	−405	200	10	47	212
Elimäki	III	17	−220	170	10	17	210

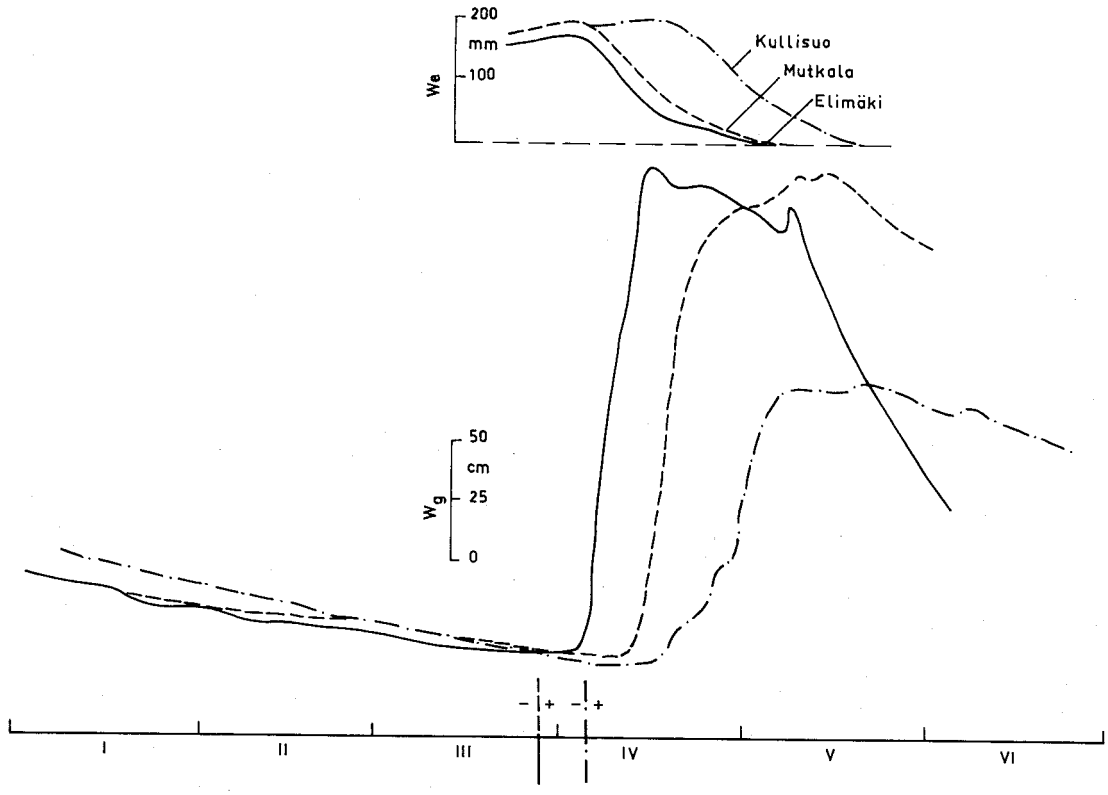

Fig. 35. Groundwater hydrographs in till soils before and after snowmelt in areas with different groundwater recharge regimes during the spring of 1984. We = water equivalent of snow, W_g = groundwater level.

soils in the different areas also corresponded rather closely to each other.

The spring of 1984 had a high snowfall in all parts of the country (see Table 2). This snow melted with record-breaking speed and rather earlier than normally (Monthly report of the Meteorological Institute 1984). The maximum values of the water equivalent of snow used in the calculations were taken from the monthly hydrological report (National Board of Waters 1984).

The groundwater reserves emptied during the winter of 1984, before the melting of snow, at almost the same rate in the different moraine regions (d_s = 10—13 cm per month). However, the reserves were recharged after the snowmelt at different rates and to different extents (Fig. 35).

The groundwater reserves were replenished most rapidly in the area of Regime III e.g. Elimäki (R_t = 17 d). The increase in groundwater level was also greatest in this area, although the water equivalent of snow was smallest (170 mm). In the most northerly areas (Regime I) the increase in groundwater level was smallest, although the water equivalent of snow (210 mm) was highest.

The different replenishment of groundwater storage as a result of melting of snow in spring in the different regions was due to differences in soil moisture. Due to the longer period of soil frost, the difference between field capacity and the water content of the soil (soil water deficit) is always greater in northern regions (Regime I) than in the south of the country (Regimes III and IV), where the soilwater and groundwater reserves reach their maximum at a later date. As a result of the soil moisture deficit, a major part of the meltwater in the northern regions goes to the replenishment of this deficit. Only after this does recharging of the groundwater reserves begin.

In southern areas the soil moisture deficit is usually smaller than in the north, because soil

Table 39. The saturation deficit index (SD_i) of soil moisture in areas with different regimes of groundwater formation in spring 1984.

Groundwater station	Regime	Soil type	SD_i
Lautavaara (50)	II (I)	sand	0.57
Kullisuo (48)	I	sandy till	0.68
Turtakangas (42)	II	fine sand	0.58
Kangaslahti (23)	II	sand	0.66
Laihia (31)	II	silt	0.79
Äijälä (35)	II	sand	0.79
Jämijärvi (10)	II (III)	sand	0.80
Oripää (7)	III	sand	0.78

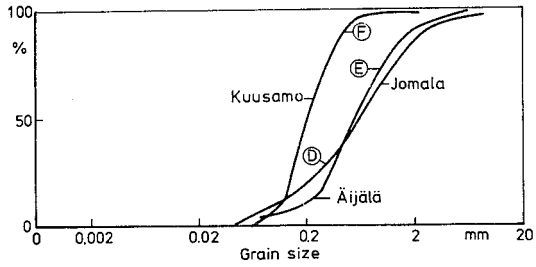

Fig. 36. Grain size distribution of representative glaciofluvial sand soils at the groundwater stations at Jomala (D), Äijälä (E) and Kuusamo (F).

water reserves are replenished until late in the autumn and often even during the winter. The effects of meltwaters are observed faster and more directly in the formation of groundwater (short R_t-time) and a relatively great proportion of the meltwater goes to groundwater formation.

The regional occurrence of soil water deficit was examined in the spring of 1984 by neutron measurements at certain groundwater stations before and after snowmelt. The soil water deficit is described by the saturation deficit index (SD_i), which in this context is the relationship between measured neutron impulses before and after melting at depths of 50, 100 and 200 cm. The number of impulses is directly proportional to the water content of the soil. The smaller was the saturation deficit index, the greater was the moisture deficit of the soil before snowmelt (Table 39).

6.22 Recharge in glaciofluvial sand aquifers

The effect of snowmelt on the level of groundwater in sand aquifers was examined in the spring of 1984 at the groundwater stations of Kuusamo (Regime I), Äijälä (Regime II) and Jomala (Regime IV). The grain-size distribution curves describing sandy soils of the different areas are presented in Fig. 36 and the geohydrological parameters used in hydrograph analysis is presented in Table 40.

As a result of effective soil porosity the groundwater reserves discharge to a greater extent in sandy aquifers than in moraine aquifers, although the rate of discharge in winter (d_s) is similar in both soil types. Correspondingly, the groundwater reserves are recharged by meltwater to a greater extent in coarser soil types, although the corrected groundwater rise (GW_r) is considerably lower than in fine-grained soils.

The reserves of groundwater emptied at the greatest rate during March in the area of Jomala

Table 40. Some geohydrological parameters of sandy soils used in hydrograph analysis (see list of symbols).

Groundwater Station	Regime	Sand %	W_g cm	We_{max} mm	d_s cm month^{-1}	R_t d	GW_r cm
Kuusamo	I	49	−230	220	10	7	100
Äijälä	II	82	−400	210	10	26	120
Jomala	III	67	−210	145	25	11	110

(Regime IV), where recharging was still taking place during January and February. Due to the later recharging of groundwater the soil moisture deficit is smaller in the area of Regime IV than in other areas before the spring thaw. As a result of the smaller soil water deficit in sandy soils the formation of groundwater after the thaw was comparatively greater in the Jomala area than in the example areas in the north of the country at Äijälä (Regime II) and Kullisuo (Regime I), although the recharging of groundwater also occurs primarily from spring meltwater in these areas (Fig. 37).

7. GEOCHEMICAL CYCLES AND THE INTERACTIONS BETWEEN MELTWATER, INFILTRATION WATER AND GROUNDWATER

The geochemical cycle on land can be characterized by four major reservoirs, namely atmosphere, biosphere, soil and rock, where water is the primary agent to move the chemical materials between them (Fig. 38).

Inputs of materials to soil and vegetation originate partly as precipitation from the atmos-

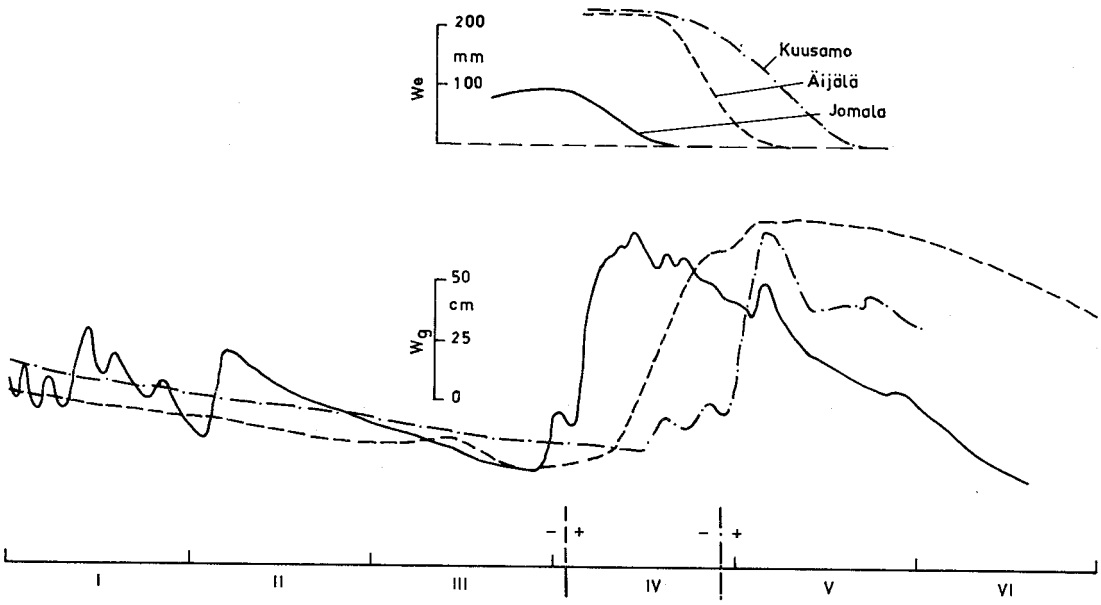

Fig. 37. Groundwater hydrographs in sandy soils before and after snowmelt in areas with different groundwater recharge regimes during the spring of 1984. We = water equivalent of snow, W_g = groundwater level.

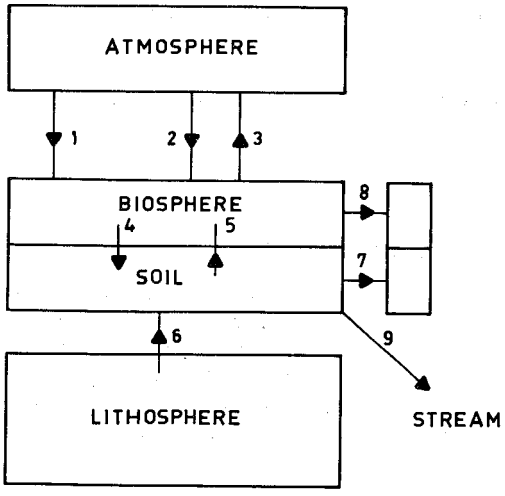

Fig. 38. Schematic cycle of some elements at the continental surface (1. atmospheric precipitation; 2. gaseous uptake and photosynthesis; 3. gaseous release; 4. leaching; 5. uptake by vegetation; 6. rock weathering; 7. increase in soil layer thickness; 8. forest increment; 9. dissolved and particulate stream outputs (Maybeck 1983)).

phere, and partly from soil as a result of weathering of bedrock.

Outputs of materials occur mainly by baseflow transport of particulate and dissolved material, but also to the atmosphere through gas emission from soil and vegetation (CO_2, NH_3, H_2S), aerosol emission from vegetation (K, SO_r), and particulate emission (dust, forest fires, etc.).

In most cases, a given element will be present in this input-output cycle in various different forms; gases, ions, molecules, dissolved and particulate organic material and inorganic particulate matter.

If a given element is not enriched by soil weathering or stored in the ecosystem, the total output should be equal to the total input. When rock weathering is low the groundwater output is greatly influenced by atmospheric inputs (Maybeck 1983).

In the following the relationship between the equivalent concentrations of certain individual ions and the ionic sum of these ions is examined in detail in meltwater, infiltration water and groundwater (Fig. 39). If the waters compared are identical in their chemical composition, the plots

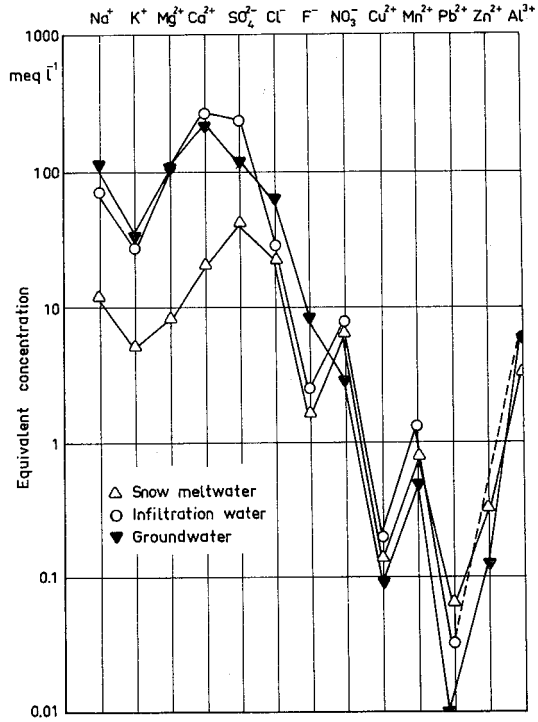

Fig. 39. The equivalent concentrations of meltwater, infiltration water and groundwater at groundwater stations.

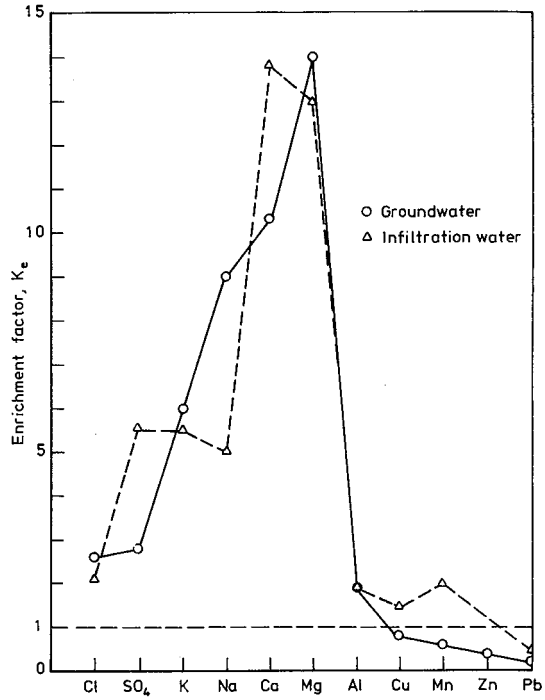

Fig. 40. The mean enrichment factors for groundwater and infiltration water at groundwater stations.

of all the components and the ionic sum line will fall on the 1:1 line (Henriksen and Kirkhusmo 1982). The concentration relationships of infiltration water and groundwater were clearly different from those of meltwater. The ionic sum line describing the concentration relations of water was clearly below the 1:1 line. Only the atmophilic chloride ion was situated close to the 1:1 line.

In the comparison of material concentrations in infiltration water and groundwater the ionic sum line almost joins with the 1:1 line. This examination also indicated that the ionic sum of groundwater in shallow aquifers is largely determined during infiltration. The composition of groundwater is thus mainly determined by processes occurring in the organic soil surface and in the unsaturated soil zone. Also the sulfate and calcium of infiltration water are partly witheld during percolation through the soil, whereas sodium and chloride, being highly soluble, are enriched in the groundwater.

The enrichment factors (K_e) were calculated between the mean substance concentrations of groundwater and infiltration water on the one hand and of meltwater on the other (Fig. 40).

If the value of K_e was greater than 1.0 the concentration in question had increased and correspondingly if K_e was smaller 1.0 the concentration had decreased after infiltration.

Unusually high values of K_e in the case of heavy metals may be indicative of the occurrence of ore deposits in the groundwater recharge area.

7.1 Chemical relations

For analysis of the phenomena and interrelations of chemical composition of meltwater, infiltration water and groundwater multivariate statistical methods were used. The results are visualized by graphical diagrams, in which several analyses of different water samples can be compared directly and quickly.

The semilogarithmic vertical scale diagrams as shown in Fig. 41 were first used extensively by Schoeller (1935). The ionic concentrations in meltwater, infiltration water and groundwater (in μeq l^{-1}), at groundwater stations were plotted in the sequence Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, F^-, NO_3^-, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+} and Al^{3+} on the

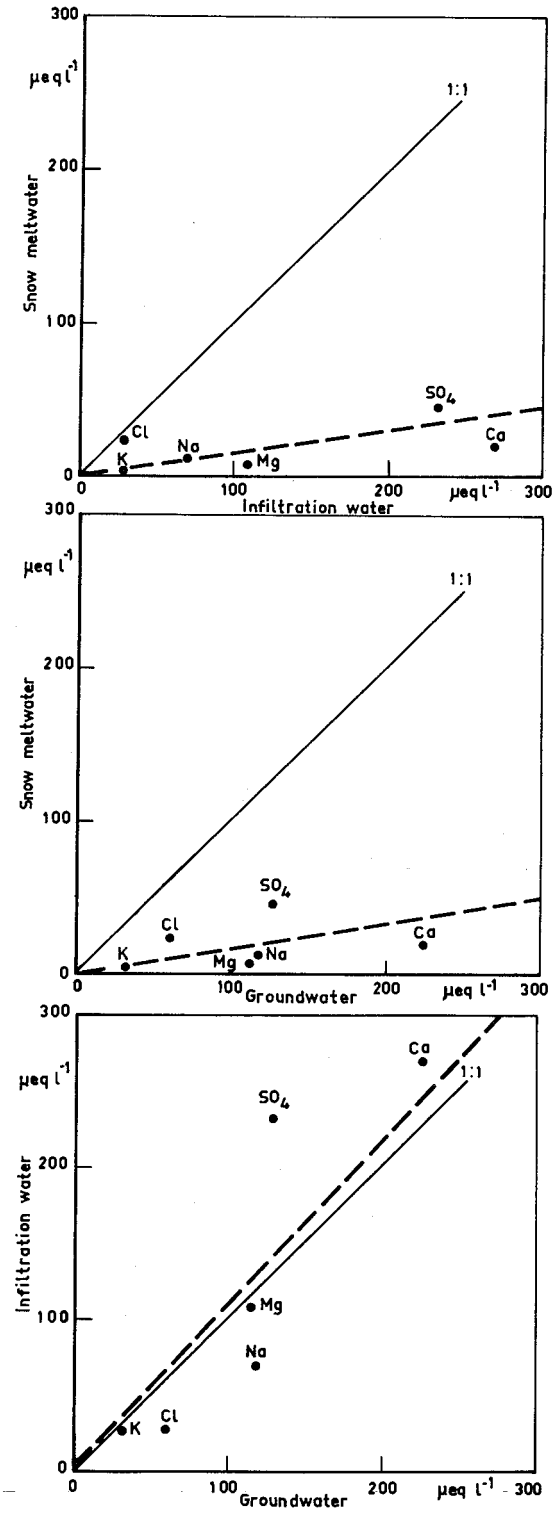

Fig. 41. The ionic ratios for mean material concentrations in meltwater, infiltration water and groundwater at different groundwater stations.

vertical axes using logarithmic scales.

The ionic relationships between meltwater, infiltration water and groundwater were examined as equivalent concentrations, which in the case of metals were calculated from the median concentrations and for other ions from the means.

Differences between ionic spectra in meltwater, infiltration water and groundwater were rather slight. The median concentrations of metals with the exception of aluminium, were greater in meltwater than in groundwater. In particular the concentration of lead was considerably greater in meltwater than in groundwater, which refers to atmophilic origin of these metals.

With the exception of nitrate, the equivalent concentrations of most other ions were significantly lower in meltwater than in infiltration water and groundwater, which refers lithophilic origin of these ions. The concentrations of various cations and anions (in meq l^{-1}) in meltwater, infiltration water and groundwater are illustrated in trilinear diagrams in two separate triangles (Fig. 42). This method of presentation was first used by Piper (1944). The samples analyzed corresponded mutually with respect to both spatial and temporal considerations, so that the groundwater and infiltration waters were formed from the meltwater of the same area.

The relative percentages of cations (except Ca) were very similar in the waters investigated, although the alkali and earthalkali metals always increase considerably after infiltration (Table 41).

Because of the lack of alkalinity on meltwater, the concentration distribution of meltwater could be clearly distinguished from that of the soil waters.

7.11 Relationships between groundwater quality parameters in different soil types

The relative proportions of material concentrations in groundwater were examined in detail in different soil types using triangle diagrams. The percentages of the cations and anions investigated were calculated on the basis of the mean equivalent concentrations at the groundwater stations. According to the results of the Piper analysis the greatest deviation between cations was in till soils, whereas in the case of anions the greatest deviation was in the coarse-grained soils (Fig. 43).

The ionic sums of cations and anions increased with increase in the fine-grained nature of the soil. The percentage relationships between individual ions did not however differ radically in the different soil types (Table 42).

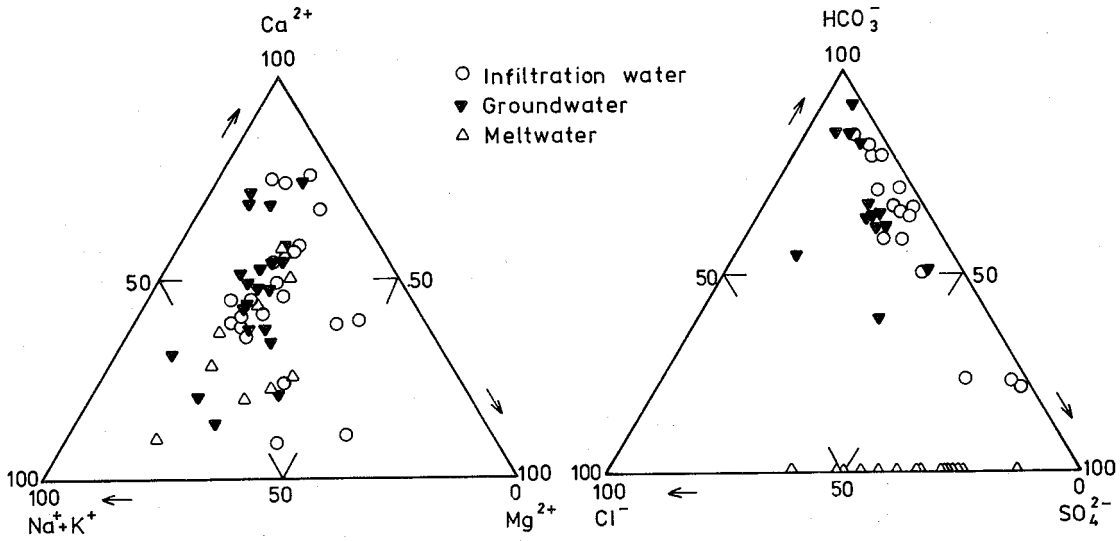

Fig. 42. Piper diagrams with cations and anions plotted separately for meltwater (△), infiltration water (O) and groundwater (▼) at different groundwater stations.

Table 41. Mean equivalent proportions of cations and anions in meltwater, infiltration water and groundwater.

Element	Σ cations				Σ anions			
	$\bar{x}$ meq l^{-1}	Ca^{2+} %	Mg^{2+} %	$Na^{+}+K^{+}$ %	$\bar{x}$ meq l^{-1}	SO_4^{2-} %	Cl^{-} %	HCO_3^{-} %
Meltwater	0.032	33.0	28.2	38.8	0.058	64.8	35.2	0
Infiltration water	0.500	45.6	27.3	27.1	0.618	34.0	5.8	60.2
Groundwater	0.371	46.4	21.0	32.6	0.343	21.9	12.5	66.6

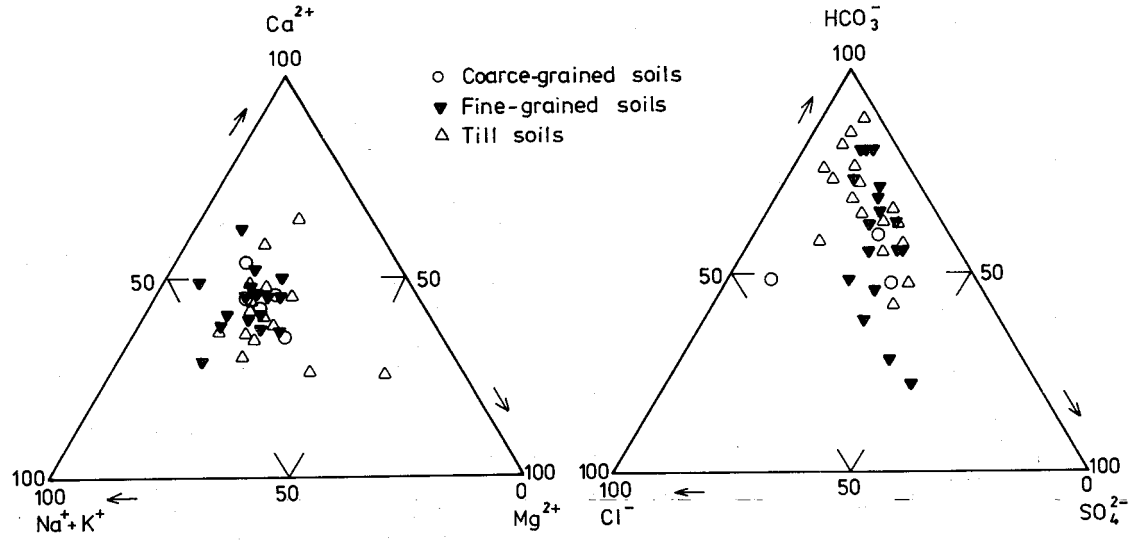

Fig. 43. Piper diagrams with separately plotted cations and anions for groundwater in coarse-grained (O), fine-grained (▼) and till (△) soils.

Table 42. Mean equivalent proportions of cations and anions in different soil types.

Soil type	n	Σ cations				Σ anions			
		x̄ meq l^{-1}	Ca^{2+} %	Mg^{2+} %	$Na^{+} + K^{+}$ %	x̄ meq l^{-1}	SO_4^{2-} %	Cl^{-} %	HCO_3^{-} %
Coarse-grained	17	0.291	44.3	20.3	35.4	0.303	26.0	15.5	58.5
Fine-grained	4	0.476	44.7	22.1	34.1	0.439	19.7	29.1	51.2
Moraine	17	0.481	41.4	25.9	32.7	0.425	19.5	13.3	67.2

7.2 Chemical relationships and their dependence on water stage

The origin of elements appearing in groundwater was defined earlier in this work as either lithophilic or atmophilic according to whether the element concentration in the groundwater is derived from atmospheric deposition or dissolution of minerals from the soil.

In the following the relative proportions of typically lithophilic elements (K, Mg, Ca and Na) and elements which at least in certain circumstances have a mainly atmophilic origin (Pb, Mn and Cu) are examined in groundwater before and after snowmelt. The elemental balance in groundwater was also compared with the concentrations in meltwater and infiltration water of the same groundwater formation basin.

The chemical relationships between meltwater, infiltration water and groundwater and the effects of groundwater height on the chemical balance were investigated in the water district of Kainuu at Kolmisoppi (45), Lumiaho (46), Alakangas (47) and Kullisuo (48). The dominant soil type at these observation sites was sand or silt moraine except at Alakangas, where the dominant soil types were sand and gravelly sand. Due to the climatic similarity of the areas the formation of groundwater occurred at approximately the same time at all the sites.

The concentrations investigated were the mean monthly concentrations for the period 1976—1980. The snow samples corresponded to cumulative winter samples and the infiltration water samples to the soil water formed due to melting and partly to spring rainfall, also (Figs. 44, 45, 46 and 47).

The concentrations of alkali and earthalkali metals were low in the meltwater. During infiltration the concentrations increased rapidly in the soil water to a level higher than that observed in the groundwater. This trend was obvious despite the irregular variations in concentrations in the annual figures.

The concentrations of heavy metals increased in the groundwater after snowmelt in the coarse-grained soil as e.g. at the Alakangas groundwater station. Similar changes were also observed at the Lumiaho and Kolmisoppi stations. The data presented in Figs. 44—47 suggest that heavy metals in groundwater are of mainly atmophilic origin in shallow aquifers and more generally in areas with pre-cambrian intrusive rock types.

The direct effects of meltwater on the metal concentrations of groundwater become most evident when investigating annual variations in concentrations. For example in Alakangas in 1982 the copper concentration of groundwater clearly increased after the melting season, attaining the same level as that observed in the meltwater and infiltration water (Fig. 46). The lead concentration of the groundwater, however, remained approximately the same throughout the year at a level well below that in the snow and in the infiltration water.

In sulfide rock areas, e.g. at the groundwater station at Kangaslahti (23), the heavy metal concentrations in groundwater vary temporally in a quite different manner. The concentrations of Mn, Cu, Pb and Zn in groundwater at Kangaslahti are mainly due to the dissolution of minerals in the bedrock. The mean heavy metal concentrations of groundwater before snowmelt during the period

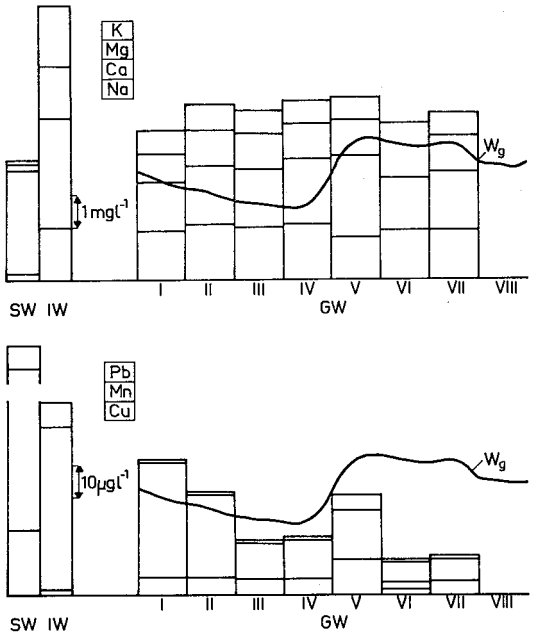

Fig. 44. The mean monthly (1976–1980) concentrations of Na, Ca, Mg, K, Cu, Mn and Pb in meltwater (SW), infiltration water (IW) and groundwater (GW) at the Kolmisoppi groundwater station.

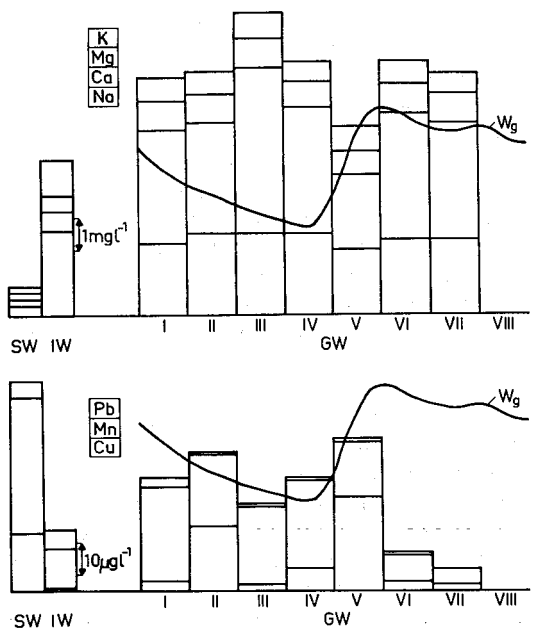

Fig. 45. The mean monthly (1976–1980) concentrations of Na, Ca, Mg, K, Cu, Mn and Pb in meltwater (SW), infiltration water (IW) and groundwater (GW) at the Lumiaho groundwater station.

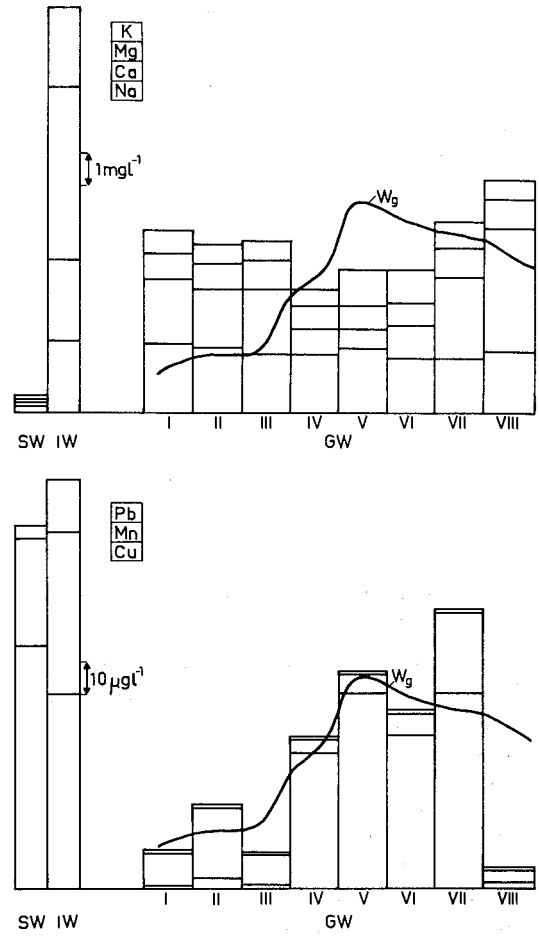

Fig. 46. The mean monthly (1976–1980) concentrations of Na, Ca, Mg, K, Cu, Mn and Pb in meltwater (SW), infiltration water (IW) and groundwater (GW) at the Alakangas groundwater station.

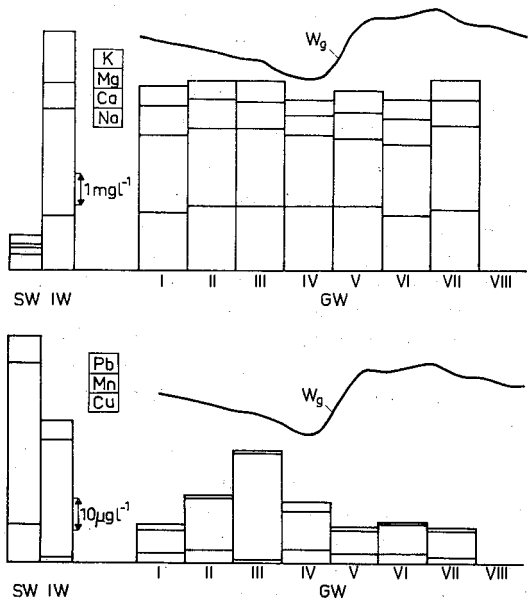

Fig. 47. The mean monthly (1976–1980) concentrations of Na, Ca, Mg, K, Cu, Mn and Pb in meltwater (SW), infiltration water (IW) and groundwater (GW) at the Kullisuo groundwater station.

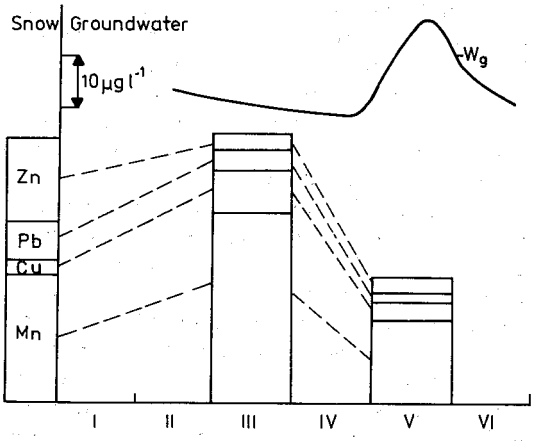

Fig. 48. Mean concentrations of zinc, lead, copper and manganese in snow and in groundwater at different heights of groundwater level (W_g) in the Kangaslahti ore field area during the period 1976–1980.

1976—1980 were clearly greater than the metal concentrations developing in snow as a result of deposition (Fig. 48). After snowmelt the metal concentrations of groundwater, were considerably diluted. In this case a lithophilic origin of groundwater metal concentrations was obvious. The heavy metals of groundwater and particularly their cyclic variations in conjunction with snowmelt may also often reflect the mineral composition of the bedrock in the groundwater formation area (Soveri 1981). The temporal variations of groundwater metal concentrations are therefore significant in prospecting for mineral ores.

Investigation of the metal concentrations of groundwater before and after snowmelt may provide important clues concerning mineral ores occurring in the region. If a metal concentration clearly decreases after the thaw, it can be assumed that the metal in question occurs in the soil or in the bedrock. Even rather small differences in concentrations may provide indications of ore deposits, because the metals in question are usually only marginally soluble in groundwater.

7.3 Influence of acid meltwater on groundwater

The acidification of surface water is a phenomenon well known to occur in the Nordic Countries and in Canada and the Eastern United States. The rapid increase in the acidity of rainwater during recent decades is generally accepted as the cause of acidification.

Particular attention has also been paid in recent years to the acidification of groundwater. Acid rain has been shown to have caused considerable changes in groundwater quality e.g. in Sweden (Aastrup and Persson 1985). Increase in the solubility of toxic metals (Pb, Cu, Cd and Al) in both soil and water distribution networks will be a real cause for concern in public health during the coming decades, particularly because future water management is expected to rely more on groundwater reserves than at present (Vesihallitus 1984 b).

The acidification of groundwater and its progression through several developmental stages can be described with the aid of the following concepts.

Groundwater influenced by acidification: Geochemical changes in the soil water system due to acid loading become detectable, elemental concentrations (e.g. Ca, Mg, SO_4, Al, Cd and Cu) increase in groundwater. No changes in water pH necessarily discernable at this stage.

Acidified groundwater: decrease in groundwater pH as a function of time.

Acid groundwater: loss of groundwater alkalinity, pH below 5.0.

In Finland the time series of water quality measurements are still too short to demonstrate that acidification of groundwater has occurred. However, the earlier indications of acidification, detailed above as "Groundwater influenced by acidification", can be demonstrated over a shorter period of time.

The mean concentrations of pH, alkalinity, calcium, magnesium, sulfate and aluminium at the groundwater stations in 1975—1976 (y) and 1982—1983 (x) have been compared in Fig. 49. Each point in the graphs represents the mean of several (10—20) individual observations. If no changes occurred in a given concentration over the period of examination, the points were situated along the 1:1 line. The following regression equations were calculated between the concentrations during the two observation periods:

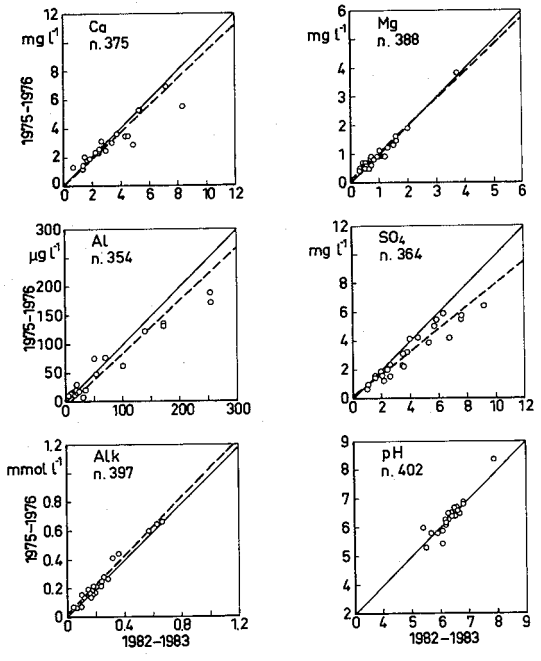

Fig. 49. Changes in calcium, magnesium, aluminium, sulfate, alkalinity and pH at the groundwater observation stations during the periods 1975–1976 and 1982–1983.

$$Ca_{(82-83)} = 1.07\ Ca_{(75-76)} + 0.04 \quad r = 0.96^{***} \quad (56)$$
$$Mg_{(82-83)} = 1.70\ Mg_{(75-76)} - 0.64 \quad r = 0.98^{***} \quad (57)$$
$$Alk_{(82-83)} = 0.94\ Alk_{(75-76)} - 0.002 \quad r = 0.98^{***} \quad (58)$$
$$SO_{4(82-83)} = 1.25\ SO_{4(75-76)} - 0.062 \quad r = 0.95^{***} \quad (59)$$
$$Al_{(82-83)} = 1.10\ Al_{(75-76)} + 7.62 \quad r = 0.98^{***} \quad (60)$$

It was quite clear that the concentrations of sulfate, calcium and aluminium in groundwater had increased between the two periods of observation (7—8 years). A particularly large change had taken place in the case of sulfate, which did not however affect the pH balance of the groundwater. The simultaneous increases in the concentrations of calcium on the one hand and sulfate on the other were apparently compensatory, so that no effect on the pH was observed.

According to t-test, the increase of sulfate concentration was significant at the 98 % confidence level. Corresponding significances for aluminium and calsium were 95 % and 90 %. At higher levels of calsium concentration (> 2,3 mg l^{-1}) the significance increased to 95 %. No statistically significant changes were observed in the case of manganese, alkalinity and pH.

Surface water and groundwater react in a different manner to the effects of acid rain. Whereas the effects of meltwater on surface waters are often seen as an immediate decrease in pH, the pH of groundwater may actually increase. In the short run the groundwater baseflow current caused by meltwater may also result in a marked neutralization effect in surface waters, with consequent increase in the pH of lake water. Groundwater flow into watercourses does in fact have a significant effect on the buffer capacity of lake waters and thus also on their ability to regulate acidity (Bottomley et al. 1984).

Groundwater in Finland is naturally slightly acidic (pH median 6.3) and its buffer capacity is low because the bedrock is composed mainly of acid crystalline rocks, mostly granite and gneiss, which are rather resistant to weathering. Shallow-lying groundwater is therefore particularly sensitive to the effects of acidification.

Prior to this investigation, pH changes had not been observed to any great extent in Finnish groundwater. However, the results of this study have shown that the concentrations of calcium, sulfate and aluminium have increased as a result of the acidification process over a rather short period of observation. This is a cause for considerable concern. These changes may predict reductions in groundwater pH in the near future, at the latest when the cation exchange capacity is exchausted and the unsaturated soil strata is no longer sufficient to buffer the hydrogen ions introduced with acidic rainfall and snowmelt waters.

8. CONCLUDING REMARKS

Groundwater is a renewable natural resource which is easily disturbed by environmental changes. The major aim of this work was to provide basic information concerning both the present status of groundwater in unpolluted regions and the climatic and geological factors affecting groundwater quantity and quality. The data provided by the investigation will also serve water management and its future development especially in sparsely populated regions, as well as the supervision of the effects of human activities on the cycling of water and materials in the atmosphere, watercourses and soil. A summary of the main results of this work is presented in the following:

1. The data was collected mainly from the groundwater stations of the National Board of Waters during the period 1976—1981, with supplementation in part by observations from 1982, 1983 and 1984. The network of 54 groundwater stations produces basic data concerning groundwater quantity and quality, their natural variations and the geohydrological factors affecting groundwater status.
2. About 15—40 % of the annual precipitation in Finland falls as snow. The water immobilized in the snow cover, as well as the materials reaching the snow by wet and dry deposition, is rapidly released during the spring thaw to the soil and also partly to the groundwater. Materials contained in the snow cover reflect the degree and nature of atmospheric loading. After melting and infiltration through the soil, they eventually affect groundwater quality.
3. The median pH value of snow was 4.6 and the mean of electrical conductivity was 2.2 mS m^{-1}. The following mean concentrations were obtained for materials in snow: SO_4 2.2 mg l^{-1}, Cl 0.8 mg l^{-1}, Na 0.3 mg l^{-1}, K 0.2 mg l^{-1}, Ca 0.4 mg l^{-1}, Mg 0.1 mg l^{-1}, N_{tot} 736 $\mu g\ l^{-1}$, P_{tot} 18 $\mu g\ l^{-1}$, Cu 6 $\mu g\ l^{-1}$, Mn 24 $\mu g\ l^{-1}$, Pb 8 $\mu g\ l^{-1}$ and Zn 15 $\mu g\ l^{-1}$.
4. The snow cover acts as a natural base for the deposition of airborne materials. The deposition of individual materials was estimated on the basis of the concentration of the material in snow, the value of the water equivalent of snow and the temporal duration of the period of deposition with the aid of the equation (2). The following mean monthly deposition values (in mg m^{-2}) were obtained for different materials:
   P_{tot} 0.5, SO_4 59, Cl 21, Na 8, K 6, Ca 11, Mg 4, N_{tot} 20 Cu 0.2, Mn 0.7, Pb 0.2 and Zn 0.4.
5. The proportion of infiltration of meltwater and annual precipitation in lysimeters varied considerably between different years in a given soil type depending on precipitation and its temporal distribution. In sorted soils 23—71 % (mean 41 %) of the meltwater filtered through the soil, whereas in unsorted soils the infiltration was 17—64 % (mean 39 %). The proportion of infiltration of the total annual precipitation was in sorted soils 35—88 % (mean 61 %) and in unsorted soils 25—46 % (mean 39 %).
   The contribution of meltwater to the total annual groundwater reserve was found to be considerably small. In sorted soils the infiltration of meltwater was only 13—44 % (mean 28 %) of the total annual infiltration. In unsorted soils the corresponding figure was 16—36 % (mean 27 %).
6. The temporal distribution of infiltration and the duration of infiltration varied between different years. Summer rainfall may have a great effect on total infiltration. The amount of rainfall in itself is not sufficient to explain the infiltration, but the temporal distribution of precipitation is also important. Changes in soil moisture regulate the relationship between precipitation and the formation of groundwater. Changes in the soil water reserve may vary according to the soil type and the depth of the unsaturated zone. Thus in certain cases even heavy rainfall may be totally absorbed into the soil water zone, from where it may be evaporated without any contact with the groundwater.
7. Snow meltwater is the primary agent of weathering and also of transport of the weathering products. When meltwater penetrates the soil profile and reaches the groundwater surface its acidity usually has decreased, due to buffering processes in the soil. The hydrogen ions are consumed in the infiltration water by the exchange base cations from the soil surfaces and by slow weathering reactions. The partial leaching of cations and their exchange with hydrogen is one of the main reasons why the pH of the lysimeter water and of the groundwater is in average 1.7 to 2.2 units higher than that of the snow meltwater. The pH median of infiltration water was 6.8 and the mean electrical conductivity was 8.6 mS m^{-1}. The following mean concentrations were obtained for materials in infiltration water: SO_4 12 mg l^{-1}, Cl 1.0 mg l^{-1}, Na 1.5 mg l^{-1}, K 1.1 mg l^{-1}, Ca 5.5 mg l^{-1}, Mg 1.3 mg l^{-1}, N_{tot} 520 $\mu g\ l^{-1}$, P_{tot} 4.5 $\mu g\ l^{-1}$, Cu 13 $\mu g\ l^{-1}$, Mn 132 $\mu g\ l^{-1}$, Pb 5 $\mu g\ l^{-1}$

and Al 92 $\mu g\ l^{-1}$.

8. By comparing the correlation coefficients between the substance concentrations in the meltwater and in the infiltration water, a rough estimate was obtained of the anthropogenic or geological cause-effect relationships of the different material balances. According to the correlations compared, the soil type has a clear effect on the relative ionic concentrations of sulfate, calcium and aluminium. Atmospheric effects on the material balances of infiltration water were clearly observable in the case of chloride and sodium.
9. Dissolution of materials from soil minerals into the soil water was found to be rather slight during the snowmelt period. The material concentrations in the infiltration water usually decreased with decreasing infiltration rate and correspondingly increasing solubility time. When the amount of infiltration was very small during the summer season the concentrations of different elements often increased due to the correspondingly long period of contact between the mineral soil and the soil water.
10. The concentrations of sulfate, copper and lead were greater in coarse and sorted soils than in unsorted soil types. These materials are all mainly of atmospheric origin. The concentrations of the typical products of weathering, namely calcium, potassium, magnesium, sodium and aluminium, were clearly greater in unsorted than in sorted soils.
11. The median of groundwater pH was 6.3 and the mean electrical conductivity was 6.0 mS m^{-1}. The following mean concentrations were obtained for materials in groundwater: SO_4 6.1 mg l^{-1}, Cl 2.1 mg l^{-1}, Na 2.7 mg l^{-1}, K 1.2 mg l^{-1}, Ca 4.5 mg l^{-1}, Mg 1.4 mg l^{-1}, NO_3–N 190 $\mu g\ l^{-1}$, NH_4–N 33 $\mu g\ l^{-1}$, PO_4–P 15 $\mu g\ l^{-1}$, Cu 7.5 $\mu g\ l^{-1}$, Mn 67 $\mu g\ l^{-1}$, Pb 4 $\mu g\ l^{-1}$, Zn 13 $\mu g\ l^{-1}$, Al 215 $\mu g\ l^{-1}$ and F 160 $\mu g\ l^{-1}$.
12. The correlations between elemental concentrations in shallow groundwater did not change significantly from those in the infiltration water, because the balance of elements in groundwater is largely determined during percolation. Correlations between metal concentrations varied considerably according to regional factors depending on the conditions of groundwater formation, deposition of metals from the air and the regional mineralogy of bedrock.
13. Cyclic changes in groundwater quality can be observed most clearly and most rapidly in shallow aquifers, in which concentration changes are often associated with the processes producing groundwater. In deep aquifers quality changes are usually slower and less extensive than in shallow aquifers. Stratification, mixing and time lag between recharge and discharge have the greatest effect on the cyclic variation of groundwater quality.
14. The influence of atmospheric impurities on groundwater quality was greatest in regions with coarse-grained soil. The greater the retention time of the groundwater in the soil and bedrock, the greater was the effect of alkaline components on the pH balance of the water, even in regions with acidic bedrock types.
15. Statistically significant differences in groundwater substance concentrations were recorded between the different bedrock groups. Concentrations were lower in areas with acidic, weathering-resistant rocks than in other areas. In regions with basic rock types the elemental concentrations of the groundwater were in most cases at a higher level.
16. The formation of groundwater in Finland varies considerably as a result of climatic factors. Seasonal variations of groundwater level depend on the rate of percolation to the aquifers. As the availability of percolation water is largely controlled by rainfall and evapotranspiration, seasonal patterns of change exist. In Finland the seasonal patterns of groundwater level can be classified into four main regime types corresponding to different climatological conditions.
17. The recharge due to snowmelt is of greatest significance in northern and central parts of Finland (Regimes I and II), where the main recharge event occurs as a result of the snowmelt in spring. The reserves of groundwater emptied at the greatest rate during March in the southern area of the country (Regime IV), where recharging was still taking place during January and February. A pattern of type III indicates a secondary decrease in groundwater level in the winter and is most frequently observed in south-western Finland and in coastal regions in the south and west of the country.
18. The relative proportions of material concentrations in groundwater were examined in detail in coarse-grained, fine-grained and till soil types using triangle diagrams. The ionic sums of cations and anions increased with increase in the fine-grained nature of the soil. The relationships between individual ions did not however differ radically in the different

soil types.

19. Groundwater in Finland is naturally rather acidic and its buffer capacity is low because the bedrock is composed mainly of acid crystalline rocks. Shallow lying groundwater is therefore particularly sensitive to the effects of acidification. To date, pH changes have not been observed to any great extent in Finnish groundwater. However, the results of this study show that concentrations of calcium, sulfate and aluminium have increased as a result of the acidification process over a rather short period of observation, which will be a cause for considerable concern in the very near future.

Continuos monitoring and long observation series are essential for the estimation and prediction of the slow changes taking place in the environment. The groundwater stations of the National Board of Waters are background stations situated in nearly natural areas. In addition to regular monitoring, integrated basic research has also been conducted on the basis of data obtained from these stations. The aim of this research, in addition to environmental monitoring, has been to assist in the development of groundwater acquisition. In the following a summary is presented of future research needs and practical possibilities for utilization brought to light in the present investigation:

A) Snow investigations should be utilized to a greater extent in air protection activities. The advantages of such investigations in the estimation of deposition include:
- ease of arrangement of regional representativity
- possibility of choosing from a wide range of different materials
- low levels of contamination during the winter season
- low costs and rapidity, because the method is based on "in situ" and does not involve its own specific equipment costs.

B) Investigations of infiltration play a central role in the estimation of changes in groundwater quality. In studies of the effects of meltwater and rainwater on the mobilization of materials in the soil, more attention should be paid to the roles of the organic surface layer and of the different soil horizons in the leaching and retainment of materials. In particular, investigation should be made of the transport of base cations, heavy metals and aluminium. Furthermore, the experiments and observations should be made in undisturbed in situ conditions, using for example infiltration bowls made of plexiglass.

C) The formation of groundwater in till soils should be examined in more detail. According to the results of this investigation on an average 39 % of the precipitation takes part in the formation of groundwater in unsorted soil types. The tills of the coastal areas constitute considerable groundwater reserves, which should be utilized more extensively, particularly in sparsely populated areas.

Changes in the metal concentrations of groundwater are usually rather slight and are in most cases associated with events taking place during the spring thaw. Even small concentration changes in groundwater before and after snowmelt may provide indications of mineral ore deposits situated in the groundwater recharge area.

ACKNOWLEDGEMENTS

The data utilized in this work was collected mainly by personnel of the various Water Districts and of local branches of the Hydrological Office. Analyses of water samples were carried out in the laboratories of the Water Districts and in the research laboratory of the National Board of Waters.

Processing of the primary data was carried out by Ms. Marianne Rajamäki, Mr. Tauno Tirronen and Ms. Kirsti Granlund, who also prepared the statistical summaries of the data.

Prof. Kalevi Kauranne and prof. Seppo E. Mustonen provided valuable comments and guidance throughout the work, for which I express my most sincere gratitude. Prof. Robert Nelson (Univ. of Wisconsin, USA), Dr. Pertti Seuna, Dr. Esko Kuusisto, Mr. Veli Hyvärinen, Ms. Kirsti Haapala, Mr. Risto Lemmelä, Mr. Juha Kämäri and Ms. Marja-Riitta Soveri all read this manuscript in its preparative stages and provided me with valuable comments and suggestions.

The manuscript was typed by Ms. Eeva-Liisa Alanne and Ms. Anja Ketonen, the figures were drawn by Ms. Tuulikki Sevón and the layout of the work was accomplished by Ms. Terttu Halme.

The text was translated by Mr. Michael Bailey, who also commented critically on certain imprecise passages in the original Finnish.

To all these people, as well as to the many others who assisted me in many ways during the preparation of this work, I express my deep-felt gratitude.

Financial support for publication was also obtained from Maa- ja vesitekniikan tuki r.y.

Finally, I would also like to thank the National Board of Waters, the Academy of Finland and the Ministry of the Environment for enabling me to take part in various relevant international congresses, which provided inspiration and encouragement for both the planning and execution of this study.

LOPPUTIIVISTELMÄ

Pohjaveden käyttö on viime vuosikymmenien aikana jatkuvasti lisääntynyt yhdyskuntien ja haja-asutusalueiden vedenhankinnassa. Vaikka pohjavesi on uusiutuva luonnonvara, sen laatu ja määrä häiriytyy helposti ympäristössä tapahtuvien muutosten vaikutuksesta.

Tämä tutkimus tarkastelee pohjaveden tämän hetkistä tilaa Suomessa luonnontilaisilla pohjaveden muodostumisalueilla sekä arvioi pohjaveden määrän ja laadun vaihteluihin vaikuttavia syitä erityisesti lumen ja roudan kevätsulamisen yhteydessä.

1. Tutkimusaineisto kerättiin pääosin vesihallituksen pohjavesiasemilta vuosina 1976—1981. Aineistoa on osittain täydennetty vuosien 1982, 1983 ja 1984 havainnoilla.
2. Noin 15—40 % Suomen alueen vuosisadannasta tulee lumena. Lumipeitteeseen sitoutunut vesimäärä ja siihen kuiva- ja märkälaskeumina kerääntyneet aineet vapautuvat kevätsulamisen jälkeen geohydrologiseen kiertoon. Lumessa esiintyvät aineet kuvastavat ilman kautta maaveden ja pohjaveden laatuun vaikuttavaa kuormitusta.
3. Ajanjakson 1976—1981 lumen sulamisveden pH:n mediaani oli 4,6 ja keskimääräinen sähkönjohtavuus 2,2 mS m^{-1}. Keskimääräiset aine pitoisuudet olivat SO_4 2,2 mg l^{-1}, Cl 0,8 mg l^{-1}, Na 0,3 mg l^{-1}, K 0,2 mg l^{-1}, Ca 0,4 mg l^{-1}, Mg 0,1 mg l^{-1}, kok. N 736 μg l^{-1}, kok. P 18 μg l^{-1}, Cu 6 μg l^{-1}, Mn 24 μg l^{-1}, Pb 8 μg l^{-1} ja Zn 15 μg l^{-1}.
4. Lumipeite toimii luontaisena laskeuma-alustana, johon ilman epäpuhtaudet kerrostuvat. Lumen ainepitoisuuden, vesiarvon ja laskeuma-aikatietojen avulla arvioitiin ainekohtaista laskeumaa. Eri aineille saatiin seuraavat keskimääräiset kuukausilaskeumat (mg m^{-2}): kok. P 0,5, SO_4 59, Cl 21, Na 8, K 6, Ca 11, Mg 4, kok. N 20, Cu 0,2, Mn 0,7, Pb 0,2 ja Zn 0,4.
5. Sulamisvedestä ja vuosisadannasta lysimetriastioihin imeytyvä vesimäärä vaihteli paljon eri vuosina myös samalla maalajialueella. Lajittuneissa maalajeissa sulamisvedestä imeytyi 23—71 % (keskimäärin 41 %) ja lajittumattomissa maalajeissa 17—64 % (keskimäärin 39 %). Koko vuoden sadannasta imeytyi lajittuneissa maalajeissa 35—88 % (keskimäärin 61 %) ja lajittumattomissa maalajeissa 25—46 % (keskimäärin 38 %). Sulamisveden osuus koko vuoden pohjaveden muodostumisesta oli hiekka- ja soramaalajeissa 13—44 % (keskimäärin 28 %) ja siltti- ja moreenimaalajeissa 16—36 % (keskimäärin 27 %).
6. Kesäsateilla saattaa olla suuri merkitys kokonaisimeyntään ja myös pohjaveden muodostumiseen. Sateen määrä ei yksin selitä imeyntää, vaan sitä merkitsevämpää on sateen ajallinen jakautuminen. Maankosteus säätelee ratkaisevasti sadannan ja pohjaveden muodostumisen välistä yhteyttä. Maan kosteusvajauksen ollessa suuri runsaatkin sateet voivat imeytyä maavesivyöhykkeeseen ja haihtua pois joutumatta lainkaan pohjaveteen.
7. Hapan sulamisvesi (pH 4,6) nopeuttaa maaperän rapautumista ja myös kuljettaa rapautumistuotteita (esim. Ca, Mg, Na ja Al) pohjaveteen. Lumen sulamisesta muodostuneen vajoveden vetyionikonsentraatio lisääntyi keskimäärin 2,2 pH-yksikköä ja pohjaveden 1,7 pH-yksikköä sulamisveteen verrattuna. Lysimetrikokeiden mukaan maaveden pH:n mediaani oli 6,8 ja keskimääräinen sähkönjohtavuus 8,6 mS m^{-1}. Keskimääräiset ainepitoisuudet olivat: SO_4 12 mg l^{-1}, Cl 1,0 mg l^{-1}, Na 1,5 mg l^{-1}, K 1,1 mg l^{-1}, Ca 5,5 mg l^{-1}, Mg 1,3 mg l^{-1}, kok. N 520 μg l^{-1}, kok. P 5 μg l^{-1}, Cu 13 μg l^{-1}, Mn 132 μg l^{-1}, Pb 5 μg l^{-1} ja Al 92 μg l^{-1}.
8. Maaveden ja pohjaveden alkali- ja maa-alkalimetallipitoisuudet sekä alumiinipitoisuus lisääntyivät selvästi suotautumisen aikana. Ilmaperäinen laskeuma vaikutti taas selvästi maaveden natrium-, kloridi- sekä eräiden raskasmetallien pitoisuuteen.
9. Aineiden mobilisaatio maaperästä on kaksivaiheinen. Lysimetrikoesarjat osoittivat, että keväällä sulamisen yhteydessä huuhtoutuu enimmäkseen talven aikana muodostuneita rapautumistuotteita ja kesällä ja syksyllä taas liuke-

nemalla vapautuneita aineita.

10. Maaveden sulfaatti-, kupari- ja lyijypitoisuudet olivat ainetasevertailujen mukaan suurelta osalta laskeumaperäisiä ja kyseiset pitoisuudet olivat yleensä suurimpia karkearakeisissa maalajeissa. Selvästi geologista alkuperää olivat taas maaveden kalsium, magnesium, natrium, kalium ja alumiini, joiden pitoisuudet yleensä lisääntyivät maalajitteiden hienorakeisuuden lisääntyessä.
11. Pohjavesiasemilla pohjaveden pH:n mediaani oli 6,3 ja keskimääräinen sähkönjohtavuus 6,0 mS m^{-1}. Keskimääräiset ainepitoisuudet olivat: SO_4 6,1 mg l^{-1}, Cl 2,1 mg l^{-1}, Na 2,7 mg l^{-1}, K 1,2 mg l^{-1}, Ca 4,5 mg l^{-1}, Mg 1,4 mg l^{-1}, NO_3–N 190 μg l^{-1}, NH_4–N 33 μg l^{-1}, PO_4–P 15 μg l^{-1}, Cu 8 μg l^{-1}, Mn 67 μg l^{-1}, Pb 4 μg l^{-1}, Zn 13 μg l^{-1}, Al 215 μg l^{-1} ja F 160 μg l^{-1}.
12. Veden suotauduttua maakerrosten läpi ja muututtua pohjavedeksi sen ainepitoisuudet yleensä jonkinverran pienenivät, poikkeuksena Cl, Na ja Al, joiden pitoisuudet suurenivat. Eri metallipitoisuuksien väliset korrelaatiot vaihtelivat alueellisesti riippuen mm. maa- ja kallioperästä, pohjaveden muodostumisolosuhteista sekä ilmaperäisestä laskeumasta.
13. Pohjaveden laadun aikavaihtelut liittyvät määrätyllä aikaviiveellä pohjavesivaraston täydentymiseen tai tyhjentymiseen. Syvissä akvifereissa pohjaveden laadun muutokset ovat hitaita ja suhteellisesti vähäisempiä kuin matalissa akvifereissa.
14. Pohjaveden määrän ja laadun vaihteluiden välillä vallitsee usein aikaero, mikä eri akvifereissa vaihtelee eri vuosina vallitsevien ilmasto-olosuhteiden mukaan. Pohjaveden kerroksellisuus, sekoittuminen ja purkautuminen vaikuttavat eniten pohjaveden laadun vaihteluihin.
15. Pohjaveden ainekonsentraatio oli yleensä pienin happamien ja parhaiten rapautumista kestävien kivilajien alueilla ja suurin emäksisten kivilajien alueilla.
16. Pohjaveden pinnan vuosivaihteluiden mukaan Suomi voidaan jakaa alueellisesti neljään regiimiin, joissa pohjaveden muodostumis- ja purkautumissuhteet selvästi poikkeavat toisistaan.
17. Sulamisveden vaikutus pohjaveden muodostumiseen oli suhteellisesti suurin Pohjois- ja Keski-Suomessa (regiimit I ja II). Eteläisillä alueilla (regiimit III ja IV) syys-sateet taas vaikuttivat eniten koko vuoden pohjaveden muodostumiseen. Ahvenanmaan (regiimi IV) ilmasto-olot ovat muuhun Suomeen nähden poikkeavat, mikä ilmenee myös erilaisena pohjaveden muodostumiskuviona.
18. Kationien ja anionien ekvivalenttipitoisuuksien ionisummat olivat siltti- ja moreenimaalajien pohjavedessä suuremmat kuin hiekka- ja soramaalajien pohjavedessä. Eri ionien suhteelliset osuudet olivat melko samat sulamisvedessä, maavedessä sekä eri maalajien pohjavedessä.
19. Lähellä maanpintaa esiintyvät pohjavedet ovat Suomessa usein luonnostaan happamia (pH mediaani 6,3) ja niiden puskurikyky on alhainen, jolloin pohjavetemme ovat myös herkkiä happamoitumisen vaikutuksille. Tarkasteltavalla ajanjaksolla ei vielä havaittu pohjavedessä pH-muutoksia. Sen sijaan kalsium-, sulfaatti-ja alumiinipitoisuudet olivat selvästi lisääntyneet jo lyhyelläkin aikavälillä. Tämä saattaa ennakoida tulevaisuudessa myös pohjaveden pH:n alenemista, viimeistään silloin, kun maaperästä liuenneet emäskationit eivät enää riitä korvaamaan happamien sulamisvesien ja sadevesien mukana huuhtoutuvia vetyioneja.

LIST OF SYMBOLS

Ac	=	acidification
Alk	=	alkalinity, mmol l^{-1}
Alk_o	=	original alkalinity
Alk_t	=	present alkalinity
a	=	empirical coefficient
c	=	cultivated land
C_s	=	snowbulk concentration, μg l^{-1}, mg l^{-1}
D_a	=	annual deposition, mg m^{-2}
D_m	=	monthly deposition, mg m^{-2}
ΔD_t	=	time of deposition; time difference (in days) between the date of sampling and the date of formation of permanent snow cover
d_c	=	groundwater depletion curve
d_s	=	depletion speed of groundwater level, cm $month^{-1}$
f	=	forest
FC	=	field capacity
GW	=	groundwater
GW_r	=	corrected groundwater rise
HW_g	=	maximum groundwater level
IW	=	infiltration water
I_a	=	total annual infiltration, mm
I_r	=	infiltration rate, mm d^{-1}
K_d	=	saturated hydraulic conductivity
K_e	=	enrichment factor

K_x = the mobility coefficient of an element x in soil water
MW_g = annual mean groundwater level
Md = median
max = maximum
min = minimum
NW_g = minimum groundwater level
n = number of analysis, observations etc.
p = peat land
P_a = total annual precipitation (uncorrected), mm
P_s = porosity of the snow pack
R_t = response time between the maximum groundwater level and the beginning of the positive daily air temperatures, in days
r_1 = correlation coefficient of snow parameters
r_2 = correlation coefficient of infiltration water parameters
r_3 = correlation coefficient of groundwater parameters
S = standard deviation
$S_{\bar{x}}$ = standard error of the mean
$S/\bar{x}$ = coefficient of variation
SD = saturation deficit
SD_i = saturation deficit index
SW = snow meltwater
s = spring
T = temperature; mean annual air temperature
t = groundwater observation tube
v = vertical flux of water
We = water equivalent of snow, mm
We_{max} = maximum water equivalent of snow, mm
W_g = groundwater level
w = observation well
$\bar{x}$ = arithmetic mean
Θ_* = effectice water content
ø = unit step function
Θ = liquid content of the snow
Θ_i = the irreducible liquid content
γ_{25} = electrical conductivity, mS m^{-1} in 25°
λ = coefficient of relative groundwater level

REFERENCES

Aastrup, M. 1979. Nederbördens betydelse för klorid och sulfat i grundvatten. p. 82—96. Vannet i Norden med IHP-nytt. Nr. 1. Nordic association for hydrology.

Aastrup, M. & Persson, G. 1984. Förändringar i grundvattnets kemi i Sverige sedan 1968. Uppsala. 30 p. Sveriges Geologiska Undersökning. Rapport september.

Aastrup, M. & Persson, G. 1985. Förändringar i grundvattnets kemi i Sverige under den senaste 15-årsperioden. Uppsala, Sverige. 10 p. SGU-rapport (in press).

Aslyng, H.L. & Hansen, S. 1982. Water balance and crop production simulation. Copenhagen. 200 p. Hydrotechnical Laboratory. The Royal Veterinary and Agricultural University. ISBN 87-88431-00-2.

Bangay, G.E. & Riordan, L. 1983. Memorandum of intent on transboundary air pollution. United States — Canada. p. 217. Work group I. Impact Assesment. Final Raport.

Barry, P.J., Brown, R.M., Cornett, R.J., Killey R.W.D., Price, A.G. & Kelly, G. 1984. Water chemistry during snowmelt in a northern basin. Kanada, Ontario. 12 p.

Beckett, P.H.T. 1964. The cation-exchange equilibria of calcium and magnesium. Soil Science. p. 118—123. Vol. 100, No. 2.

Bengtsson, L. 1982. Percolation of meltwater through a snowpack. The Netherlands. p. 73—81. Cold Regions Science and Technology, 6.

Bergkvist, B. 1980. Hydrologi-markanvändning-vattenkvalitet. In: Tungmetallers rörlighet i mark vid försurning. Stockholm. p. 79—84. Naturvårdsverket, SNV pm 1455.

Bergström, S., Carlsson, B., Sandberg, G. & Maxe, L. 1985. Integrated modelling of runoff, alkalinity and pH on a daily basis. Denmark. 25. Nordic hydrology, No 2. (in press).

Bjor, K. & Teigen, O. 1980. Effects of acid precipitation on soil and forest. In: Lysimeter experiment in greenhouse. Norway. p. 200—201. Int. conf. ecol. impact acid precip. SNSF project.

BMDP 1983. BMDP Statistical Software. University of California Press. 733 p. ISBN 0-520-04408-8.

Bottomley, D.J., Craig, D. & Johnston, L.M. 1984. Neutralization of acid runoff by groundwater discharge to streams in Canadian precambrian shield watersheds. The Netherlands. p. 1—26. Journal of Hydrology 75.

Bowen, N.L. 1928. The evolution of igneous rocks. Princeton University Press. 332 p.

Brink, N. 1981. Växtnäringsläckage från små åkermarksområden. Stockholm. p. 117—124. Naturvårdsverket, rapport snv pm 1455.

Buch, K. 1960. Zusammensetzung des Atmosphärischen Niederschlages in Finnland. p. 1—26. Societas Scientiarum Fennica XXIV 10.

Colbeck, S.C. 1981. A simulation of the enrichment of atmospheric pollutants in snow cover runoff. p. 1383—1388. Water Resources Research, Vol. 17, No. 5.

De Haan, F.A.M. 1976. Interaction-mechanismus in soil as related to soil pollution and groundwater quality. Wageningen. p. 34—51. Institute for Land and Water

Management Research. Technical Bulletin 95.

Ekholm, M. and Solantie, R. 1985. Water balance in Finland during the period 1961—1975 as compared to 1931—1960. Helsinki. p. 24—47. National Board of Waters, Finland. Publications of the Water Research Institute, 59. ISBN 951-46-8749-3, ISSN 0355-0982.

Elder, C.F. 1981. Chemistry of precipitation: Its importance to eastern Canada. New York. 13 p. ASCE, preprint 81—134.

Elgmork, K., Hagen, A. & Langeland, A. 1973. Polluted snow in southern Norway during the winters 1968—1971. p. 41—52. Environ. Poll. 4.

Engelen, G. 1981. A systems approach to ground water quality. The Netherlands. p. 1—25. Quality of groundwater. Studies in Environmental Science 17, Vol. 21. ISBN 0-444-42022-3.

Englund, J.-O. & Myhrstad, J.A. 1980. Groundwater chemistry of some selected areas in southeastern Norway. Denmark. p. 33—54. Nordic hydrology, Vol. 11, No. 1.

Englund, J.-O. 1983. Chemistry and flow patterns in some groundwaters of southeastern Norway. Norges geologiske undersøkelse. p. 221—234. Universitetsforlaget NGU 380.

Englöv, P. 1981. Nitrat in grundvatten. Resultat från ett par grundvatten-utredningar. Stockholm. p. 155—158. Naturvårdsverket, rapport snv pm 1455.

Eriksson, E. 1981. Aluminium in groundwater, possible solution equilibria. Denmark. p. 43—50. Nordic hydrology, Vol. 12, No. 1.

Erkomaa, K. & Mäkinen, I. 1975. Vesihallinnon vesitutkimuksissa käytettävistä analyysimenetelmistä. Helsinki. 41 p. Vesihallitus. Tiedotus 85. ISBN 951-46-1560-3.

Finnish Meteorological Institute, 1976—1981. Kuukausikatsaus Suomen ilmastoon. ISSN 0303-2485.

Garrels, R.M., Mackenzie, F.T. & Hunt, C. 1975. Chemical cycles and the global environment. Los Altos, California. William Kaufmann Publisher.

Gjessing, Y. & Gjessing, E.T. 1975. Snees kjemiske sammensetning som indikator på luftforurening. 18 p. SNSF-projectet TN 7/75.

Colbeck, S.C. 1981. A simulation of the enrichment of atmospheric pollutants in snow cover runoff. p. 1383—1388. Water Resources Research, Vol. 17, No. 5.

Gottschalk, L. & Nordberg, L. 1977. Mathematical modelling of groundwater level response in different geological environments. Stockholm. F SGU, C 728.

Gustafsson, Y. 1968. The influence of topography on ground water formation. Stockholm. p. 3—21. Ground Water Problems. Wenner-Gren Center International Symposium Series. Vol. 11.

Haapala, K. 1972. Sadeveden laatu Suomessa. Helsinki. 49 p. Summary: The quality of rainwater in Finland according to observations made during 1971. Vesihallitus. Tiedotus 26.

Hackbarth, D. 1981. Natural temporal variations in the chemistry of shallow groundwater, Athabasca Oil Sands area. Alberta. p. 1599—1608. Canadian Journal of Earth Sciences. Vol. 18, No. 10.

Harris, R.C. & Hohenemser, C. 1978. Mercury. Measuring and managing the risk. p. 25—36. Environment, Vol. 20, No. 9.

Harvey, H.H., Pierce, R.C., Dillon, P.J., Kramer, J.P. & Whelpdale, D.M. 1981. Acidification in the Canadian aquatic environment. Ontario. 369 p. Nat. Res. Council Canada Report No. 18475.

Hem, J.D. 1972. Chemistry and occurrence of cadmium and zinc in surface water and groundwater. The American Geophysical Union. p. 661—679. Water Resources Research, Vol. 8, No. 3.

Henriksen, A. 1979. A simple approach for identifying and measuring acidification of freshwater. p. 542—545. Nature, 278.

Henriksen, A. & Kirkhusmo, L.A. 1982. Acidification of groundwater in Norway. Denmark. p. 183—192. Nordic hydrology, 13.

Hibberd, S. 1984. A model for pollutant concentrations during snow-melt. p. 58—65. Journal of Glasiology. Vol. 30, No. 104.

Huisman, L. 1981. Groundwater pollution. In: Quality of groundwater. The Netherlands. 6 p. Studies in environmental science 17, Vol. 21. ISBN 0-444-42022-3.

Hydrological yearbooks 1976—1981. Hydrological Office, Helsinki. ISBN 951-46-6069-2, ISBN 0356-4053.

Hyvärinen, V. 1977. Statistical analysis of discharge data. Helsinki, National Board of Waters, Finland. 22 p. Publications of the Water Research Institute, 22. ISBN 951-46-3166-8, ISSN 0355-0982.

Hyyppä, J. 1973. Maamme pohjavesien geokemiasta. Summary: On Finnish groundwater geochemistry. Helsinki. p. 1—3. Papers of the Engineering-Geological Society of Finland 8, 60.

Hyyppä, J. 1981. Kemiallisten analyysien käytöstä vesien ja sorien tutkimuksessa. Helsinki. Geologi 3.

Jacks, G. 1973a. Geokemiska synpunkter på fluorid i grundvatten. Swedish Dental J. 66: 2.

Jacks, G. 1973b. Chemistry of some groundwaters in igneous rocks. Denmark. p. 207—236. Nordic Hydrology, Vol. 4, No. 4.

Jacks, G. 1978. Groundwater chemistry at depth in granites and gneisses. Kungl. Tekniska Högskolan, Stockholm. 28 p. KBS teknisk rapport, 88.

Jacks, G., Knutsson, G., Maxe, L. & Fylkner, A. 1984. Effect of acid rain on soil and groundwater in Sweden. p. 94—113. In: Pollutants in porous media. Springer-Verlag.

Jacobsen, J. & Kelstrup, N. 1981. Belysning af sammenhangen mellem grundvandskemi og geologi, København. 54 p. Dansk komite for hydrologi. Rapport, SUSÅ-H 8.

Johannesen, M. & Henriksen, A. 1978. Chemistry of snow meltwater: changes in concentration during melting. The American Geophysical Union. p. 615—619. Water Resources Research, Vol. 14, No. 4.

Johansson, I. (ed.) 1984. Nordic Glossary of Hydrology. English-Danish-Finnish-Icelandic-Norwegian-Swedish with definitions in English. Stockholm, Sweden. 224 p. KOHYNO.

Johansson, S. & Soveri, U. 1965. Grundvattenytans variation i Finland under åren 1961—1963. Summary: On variations in the groundwater level in Finland during the years 1961 to 1963. Helsinki. 36 p. Valtion teknillinen tutkimuslaitos. Tiedotus. Sarja 111, Rakennus 88.

Järvinen, O. & Haapala, K. 1980. Sadeveden laatu Suomessa 1971—1977. Summary: The quality of wet and dry deposition in Finland according to observations made from 1971 to 1977. Helsinki. 102 p. Vesihallitus. Tiedotus 198. ISBN 951-46-5055-7, ISSN 0355-0745.

Kauranne, L.K., Lindberg, E. & Lyytikäinen, E. 1961. Heavy metals in prospecting. C.R. Soc. Géol. Finlande. p. 455—472. Vol. 33.

Kauranne, L,K., Salminen, R. & Äyräs, M. 1977. Problems of geochemical contrast in Finnish soils. Helsinki. p. 34—35. In: Prospecting in areas of glaciated terrain. The Institution of Mining and Metallurgy. ISBN 0-900488-38-7.

Knutsson, G., Jacks, G., Maxe, L. & Lundberg, L. 1981. Grundvatten och försurning i Kronobergs län. Stockholm. 104 p. Kungliga tekniska högskolan. Meddelande 3: 41.

Koljonen, T., Lahermo, P. & Carlson, L. 1976. Origin, mineralogy and chemistry of manganiferous and ferruginous precipitates found in sand and gravel deposits in Finland. Finland. p. 115—135. Bull. Geol. Soc. 48.

Konoplyantsev, A.A. 1970. Evaluation of the ground water balance of large territories. IAHS-Unesco. Symposium on world water balance. Publication 92, Vol. 1.

Korhonen, K.-H. & Gardemeister, R. 1975. Maalajien kaivuluokitus. Otaniemi. 80 p. VTT, Geotekniikan laboratorio, tiedonanto 1. ISBN 951-38-0275-2.

Kristensen, K.J. 1970. Jordens vandinhold. Danmark. Hydroteknisk laboratorium.

Kříž, H. 1972. Statistical processing of long-term observations of groundwater. Amsterdam. p. 17—37. Journal of Hydrology, Vol. XVI, No. 1.

Kulmala, A., Estlander, A., Leinonen, L., Ruoho-Airola, T. & Säynätkari, T. 1982. Ilman laatu Suomen taustaasemilla 1970-luvulla. Summary: Data long-range transport measurement stations. Helsinki. 159 p. Ilmatieteen laitoksen tiedonantoja No. 36.

Kurtz, L.T. & Melsted S.W. 1972. Movement of chemicals in soils by water. University of Illinois. p. 231—239. Soil Science. Vol. 115, No. 3.

Kuusisto, E. 1984. Snow accumulation and snowmelt in Finland. Helsinki, National Board of Waters, Finland. 149 p. Publications of the Water Research Institute, 55. ISBN 951-46-7494-4, ISSN 0355-0982.

Laaksonen, R. 1975. Vesistöjen veden laadun muutoksista vuosina 1962—1973. Summary: Changes in water quality in Finnish lakes and rivers 1962—1973. Helsinki, National Board of Waters, Finland. 64 p. Publications of the Water Research Institute, 12. ISBN 951-46-1913-7.

Lahermo, P. 1970. Chemical geology of ground and surface waters in Finnish Lapland. 106 p. Bull. Comm. geol. Finlande 242.

Lahermo, P. & Rainio, H. 1972. Geologisten tekijöiden vaikutuksesta vesien fluoripitoisuuteen. Summary: On the influence of geological factors on the fluoride contents of waters. p. 8—16. Organon Dentale No 4.

Lemmelä, R. 1972. Measurements of evaporation — condensation and melting from a snow cover. p. 670—679. AHS Proceedings of the Banff Symposia 1.

Lemmelä, R. 1976. Water balance in sandy areas. Reykjavik. Nordic Hydrological Conference.

Matthess, G. 1982. The properties of groundwater. United States of America. 406 p. ISBN 0-471-08513-8.

Maybeck, M. 1983. Dissolved loads of rivers and surface water quantity/quality relationships. In: Atmospheric inputs and river transport of dissolved substances. p. 173—192. IAHS Publication No. 141.

May, H.M., Helmke, P.A. & Jackson, M.L. 1979. Gibbsite solubility and thermodynamic properties of hydroxyl — aluminium ions in aqueous solution at 25°C. p. 861—868. Geochim. et cosmochim. Acta 43.

Morel, E.H. & Wright, C.E. 1978. Methods of estimating natural groundwater recharge. Reading. p. 20. Central water planning unit. Technical note No. 28. ISBN 0-904839-36-2.

Mustonen, S. 1963. Kesäsateiden aiheuttamasta valunnasta. Summary: On the runoff due to summertime rainfall. Helsinki. 90 p. Soil and Hydrotechnical Research Office, Report 3.

Mäkinen, I. 1980. Raskasmetallipitoisuudet virtapaikoilla vuosina 1977, 1978 ja 1979. Helsinki. 33 p. Vesihallituksen monistesarja. No. 24.

NAPAP 1983. Annual Report 1983 to the President and Congress. Washington, D.C. 72 p. National Acid Precipitation Assessment Program.

Niemi, A. 1976. Concentrations and sources of some heavy metals in the coastal sea areas and inland waters around Kokkola, Central Ostrobothnia. Oulu. p. 11—16. Bothnian Bay symposium. Acta Univ. Oulu A. 42, Biol. 3.

Nordberg, L. & Persson, G. 1976. On the regional and temporal groundwater variations in Sweden. Reykjavik. 19 p. Nordisk Hydrologisk Konferense.

Nordberg, L. & Soveri, J. 1978. Seasonal and multiannual changes of groundwater storage in Norden and the adjacent part of the USSR. Hanasaari. p. 136—144. Nordic Hydrological Conference.

Nordlund, N. 1982. On the dispersion of airborne pollutants with particular emphasis on sulfur in the air over Finland. Helsinki. 18 p. ISBN 951-99359-3-2.

Oden, S. 1968. Nederbördens och luftens förorening — dess orsaker, förlopp och verkan i olika miljöer. 68 p. Swedish Nat. Sci. Res. Council, Ecology Committee, Bull. No. 1.

Olsson, T. 1980. Ground-water level fluctuations as a measure of the effective porosity and ground-water recharge. Uppsala. 46 p. SGU, rapporter och meddelanden nr 21.

Overrein, L.N. 1972. Sulphur pollution, patterns observed; Leaching of calcium in forest soil determined. p. 145—147. Ambio, Vol. 1, No. 4.

Pettijohn, F.J. (ed.) 1975. Sedimentary Rocks. New York. 628 p.

Pettyjohn, W.A. 1976. Monitoring cyclic fluctuations in groundwater quality. Las Vegas, Nevada. p. 472—480. Ground Water 14: 6.

Pierson, D.C. & Taylor, C.H. 1981. Comparative differences in the chemistry of snowpack and bulk precipitation samples collected as snow and rain. Ontario. 10 p. Department of Geography, Trent University Peterborough.

Piper, A.M. 1944. A graphic procedure in the geochemical interpretation of water analyses. Washington, D.C. p. 914—928. Trans. Am. Geophys. Union, 25.

Postma, D. 1980. Årtidsvariationer i pyrit- og siderit-förvitringsprocesser i sedimenter fra Skjernådeltact. DGU-rapport.

Pratt, P.F., Jones, W.W. & Hunsaker, V.E. 1972. Nitrate in deep soil profiles in leaching relation to fertilizer rates and volume. I. Environ. Qual 1:

Rankama, K. & Sahama, Th. 1950. Geochemistry. The University of Chicago Press. 912 p.

Ravera, O. 1974. Lead pollution in air and water.

Helsinki. p. 46—54. FEG. Informationsblatt Nr. 21. ISBN 951-46-1345-7.

Reuna, M. 1979. Annual hydrographs and duration curves of water level. Helsinki, National Board of Waters, Finland. 87 p. Publications of the Water Research Institute 33. ISBN 951-46-4444-1, ISSN 0355-0982.

Reuss, J.O. 1976. Chemical and biological relationships relevant to the effect of acid rainfall on the soil — plant system. p. 701—813. USDA Forest Service Gen. Tech. Report NE-23, Columbus, OH.

Richter, W. & Lillich, W. 1975. Abriss der Hydrogeologie, Stuttgart. 281 p. ISBN 3-510-65063-8.

Rönkä, E. 1983. Drilled wells and groundwater in the precambrian crystalline bedrock of Finland. Helsinki, National Board of Waters, Finland, 57 p. Publications of the Water Research Institute 52. ISBN 951-46-6725-5, ISSN 0355-0982.

Salmi, M. 1969. Tievarsien saastuminen Suomessa. Summary: Contamination of roadsides in Finland. p. 229—232. Terra, Vol. 81.

Schoeller, H. 1935. Utilité de la notion des échanges de bases pour la comparaison des eaux souterraines. Paris. p. 651—657. Bull. Soc. Géol. Fr., 5.

Schwartz, F. 1974. The origin of chemical variations in groundwater from a small watershed in Southwestern Ontario. p. 893—904. Canadian Journal of Earth Sciences, Vol. 11, No. 7.

Seip, H.M. 1980. Acid snow — snowpack chemistry and snowmelt. New York. p. 77—91. Central Institute for Industrial Research.

Seip. H.M. & Tollan, A. 1985. Facets of Hydrology, Vol. II. Ed. Rodda. In: Acid deposition. p. 69—98. John Wiley & Sons Ltd.

Semb, A. 1978. Deposition of trace elements from the atmosphere in Norway. Norway. 28 p. SNSF-project. FR 13/78. ISBN 82-90153-58-9.

Seuna, P. 1983. Infiltration and its dependence on some physiographic factors. Helsinki, National Board of Waters, Finland. p. 29—40. Publications of the Water Research Institute 50. ISBN 951-46-6723-9, ISSN 0355-0982.

Sillanpää, M. 1982. Micronutrients and nutrient status of soil: Global study. Rome. 440 p. FAO, 15 XIV. Soils Bulletin, Vol. 48.

Smirnow, S. 1954. Die Oxydationszone sulfidischer Lagerslätten. Berlin. 312 p. Academic Verlag.

Solantie, R. 1977. Lumipeiteajasta Suomessa. Summary: On the persistence of snow cover in Finland. Helsinki. 68 p. Ilmatieteen laitos, tutkimusseloste No 60.

Solantie, R. 1978. Characterization of the Finnish Hydrological Regime by hydrological zones. Helsinki. p. 100—109. Nordic Hydrological Conference. Hanasaari, 31.7.—3.8.1978.

Solantie, R. 1981. Lumipeitteen vesiarvon vuotuinen maksimi ja sen ajankohta. Helsinki. p. 21—22. Vesitalous 5.

Soveri, J. 1970. Ytlagrens yttorkning och vatteninnehållet hos finkorniga sediment. Lund. p. 331—339. Nordisk hydrologisk konferens, Stockholm, Vol. 2.

Soveri, J. 1972. Maavedestä, sen tutkimuksesta ja tutkimustavoitteista vesihallinnossa. Summary: On the soil water, how it is measured and on the aim of soil water investigations in the Water Adminstration. Helsinki. p. 328—330. Rakennustekniikka No 5.

Soveri, J. 1973. Pohjaveden korkeuden valtakunnallisesta havainnoinnista ja sen uudelleen järjestelyistä vesihallituksessa. Summary: National observation of groundwater stages and its reorganisation at the National Board of Waters. Helsinki. 6 p. Vesitalous 1.

Soveri, J. 1975. Vesihallituksen pohjavesiasemaverkko ja tutkimustavoitteet. Summary: Groundwater network and the aims of study. Helsinki, Insinöörijärjestöjen Koulutuskeskus. 8 p. INSKO 125-75 XIV.

Soveri, J. & Varjo, M. 1977. Roudan muodostumisesta ja esiintymisestä Suomessa vuosina 1955—1975. Summary: On the formation and occurrence of soil frost in Finland 1955 to 1975. Helsinki, National Board of Waters, Finland. 66 p. Publications of the Water Research Institute 20. ISBN 951-46-3118-8, ISSN 0355-098.

Soveri, J. 1980. Ilman laskeumat kasviravinteina. Summary: Fall-out nutrients. Helsinki. p. 639—644. Ympäristö ja Terveys, No 9—10.

Soveri, J. 1981. On the concentrations of certain substances in the meltwater and the groundwater in Finland. Amsterdam. p. 777—784. In: Quality of Groundwater. Studies in Environmental Science 17. ISBN 0-444-42022-3.

Soveri, J. & Soveri, M.-R. 1981. On fluoride and chromium concentrations in groundwater in Finland. Helsinki. p. 511—520. A Nordic Symposium on Soil-Plant-Animal-Man Interrelationships and Implications to Human Health. Mineral Elements' 80. ISBN 951-99301-2-4.

Soveri, J. (ed.) 1982. Acid groundwater in the Nordic Countries. 29 p. Nordic Hydrological Programme. NHP-Report, No 3.

Steenvoorden, J.H.A.M. 1976. Nitrogen, phosphate and biocides in groundwater as influenced by soil factors and agriculture. The Hague. p. 52—69. Groundwater Pollution. Committee for hydrological research TNO, No. 21.

Stewart, D.A. 1970. A look at agricultural practices in relation to nitrate accumulation. Nutrient mobility in soils. Report.

Stevenson, F.J. 1975. Binding of metal ions by humic acids. Second Int. Symp. Environm. Biogeochem. Burlington, Ontario. Canada Centre for Inland Waters.

Stumm, W. & Morgan, J.J. 1981. Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters. 2nd Ed. United States of America. 780 p. ISBN 0-471-04831-3.

Tanskanen, H. 1977. Soiden pintaturpeen sisältämän lyijyn alueellisesta jakautumisesta Suomessa. Summary: Lead in surface peat layer in different parts in Finland. p. 51—52. Suo, 28. (3).

Thornton, J.D., Eisenreich, S.J., Munger, J.W. & Gorham, E. 1981. Trace metal and strong acid composition of rain and snow in northern Minnesota. p. 261—282. In: Atmospheric pollutants in natural waters. Chapter 14.

Tiittinen, R. 1981. Vesien happamuuteen vaikuttavista tekijöistä alunamaa-alueilla. Helsinki. 53 p. Vesihallituksen monistesarja. No 69.

Ulrich, B. & Pankrath, J. (eds.) 1983. Effects of accumulation of air pollutants in forest ecosystems. p. 127—147. D. Reidel Publ. Co.

Vainio, E. 1984. Typpiyhdisteet maatalousalueiden kaivovesissä. Helsinki. 62 p. Vesihallituksen monistesarja, No 240.

Vesihallitus, 1976. Maa- ja pohjavesisanasto. (Soil water and Groundwater Terminology.) Helsinki. 142 p. Publications of National Board of Waters 18. ISBN 951-46-2066-6.

Vesihallitus, 1984a. Hydrologiset havainto- ja mittausmenetelmät. Helsinki. 88 p. Publications of the National Board of Waters 47. In Finnish. ISBN 951-46-7491-x, ISSN 0355-9297.

Vesihallitus, 1984b. Vesihuoltolaitokset 31.12.1982. Summary: Water supply and sewer systems 31.12.1982. Helsinki. 221 p. Vesihallitus. Tiedotus 240. ISBN 951-46-7489-8, ISSN 0355-0745.

Viro, P.J. 1953. Loss of nutrient and the natural nutrial balance of the soil in Finland. Helsinki. Comm. Inst. Forest. Fenn. 41.2.

Wickman, F.E. 1944. Some notes on the geochemistry of elements in sedimentary rocks. Stockholm. p. 1—7. Ark. Kem., Mineral. Geol., 19 B, 2.

Wiklander, L. 1978. Interaction between cations and anions influencing adsorption and leaching. Sweden, Uppsala. 15 p. The Swedish University of Agricultural Sciences.

Wright, R. & Dovland, H. 1978. Regional survey of the chemistry of the snowpack in Norway, late winter 1973, 1974, 1975 and 1976. Great Britain. p. 1755—1768. Atmospheric Environment, Vol. 12.

Zalzberg, E.A. 1977. Mnogoletnij rezhim orovnya gryntovȳh vod zonȳ izbȳtochnogo yvlazheniya evropejskoj territorii CCCP. Izvestiya vsesoyoznogo geograficheskogo obshchectva. Tom 109.